Synthesis and Solution Properties of some Polysulfobetaines

by

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DEDICATED TO MY FATHER

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ABSTRACT

FULL NAME: MOHAMMAD ABU JAFAR MAZUMDER

TITLE OF STUDY: SYNTHESIS AND SOLUTION PROPERTIES OF SOME POLYSULFOBETAINES

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The reaction of diallylamine with 1,3-propanesultone led to the synthesis of the zwitterionic monomer 3-(*N, N*-diallylammonio) propanesulfonate. The sulfobetaine was cyclopolymerized in water in the presence of sodium chloride using *t*-butylhydroperoxide as an initiator to afford a polysulfobetaine (PSB) in very good yield. The PSB, upon treatment with sodium hydroxide, was converted into an anionic polyelectrolyte (APE). While the APE was found to be readily soluble in salt-free water, the PSB needed the presence of low molecular weight salts (e.g., NaCl, KI etc, in the range 0.135-1.04 N) for its dissolution. The solution properties of the PSB and APE were studied in some detail by potentiometric and viscometric techniques. Basicity constant of the amine is found to be apparent and as such follow the modified Henderson-Hasselbalch equation; as the degree of protonation (α) of the whole macromolecule increases, the protonation of the amine nitrogens becomes increasingly more difficult. The composition and phase diagram of the aqueous two-phase systems of APE/PSB and poly(ethylene glycol) (PEG) were studied.

A special monomer, sodium *N*- (3- sulfopropyl)- 3- (*N, N* diallyl amino) propane sulfonate, containing the electrolytic as well as zwitterionic feature incorporated within same molecule, was synthesized. The monomer underwent free radical polymerization in aqueous medium using *t*-butylhydroperoxide as an initiator to give the corresponding homopolymer, poly(electrolyte-zwitterions) (PEZ). The copolymer of this electrolyte-zwitterionic monomer with sulfur dioxide was synthesized in dimethyl sulfoxide (DMSO) using azo-bis-isobutronitile (AIBN) as an initiator. The solution properties of these polymers were discussed in detail. Both the homo and copolymer were found to be readily soluble in water; thus demonstrating the electrolytic behaviour of the PEZs. The PEZs showed polyelectrolytic viscosity behaviour; the intrinsic viscosity values decreased by increasing the ionic strength of its aqueous solutions.

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DHAHRAN, SAUDI ARABIA.

ملخص الرسالة

الاسم : محمد أبو جعفر مازمدر

عنوان الرسالة : تحضير ودراسة خصائص المحلول لبعض مبلمرات البولي بيتاينات

التخصص : كيمياء

التاريخ : مايو / 2003م

أنتج تفاعل ثنائي أليل أمين مع 3،1 – بروبان سلتون مونمر ذا شحنة سالبة ومزدوجة . وقد تمت بلمرة حلقية لهذا المونمر في وسط مائي بوجود كلوريد الصوديم وباستخدام رباعي بيوتيل هيدروبروكسيد كبادئ للتفاعل ، بالمعالجة بهيدروكسيد الصوديوم PSB بمردود جيد جداً ، وتم تحويل (PSB)ونتج عن ذلك متضاعف سلفوبيتين يذوب بسهولة في الماء الخالي من الملح بينما APE ، وقد وجد أن (PAE)على متضاعف الكتروليتي أنيوني إلى وجود أملاح ذات وزن جزيئي منخفض (مثل كلوريد الصوديوم ويوريد البوتاسيوم في PSBيحتاج احلال بقياس فرق الجهد APE و PSBمدى 0.135 – 1.04 مكافئ) . وقد أجريت دراسة تفصيلية لخصائص محاليل وقياسات اللزوجة ، ولقد وجد أن الثابت القاعدي للأمين يكون ظاهرياً ويتبع معادلة هندرسون – هاسيلبالتش المعدلة ، فكلما ازدادت إضافة أيون الهيدروجين الموجب للبوليمر ازدادت صعوبة إضافة أيون هيدروجين موجب مع PSB و APEللأمين. كذلك تمت دراسة الرسوم البيانية للتركيب في نظام محلول مائي ثنائي الظور لكل من متضاعف الأيثيلين جليكول.

تم تحضير مونمر خاص يحتوي سمات اليكتروليتية وزويتر أيونية (أي مشحونة سالباً وموجباً) في نفس الجزيئ. ، كما تم (PEZ)وقد تمت بلمرة هذا المؤتمر في وسط مائي ، ونتج عن ذلك متضاعف اليكتروليتي – زيوترأوني بأستخدام (DMSO)بلمرة مزدوجة لهذا المونمر مع ثاني أكسيد الكبريت في وسط ثنائي ميثيل سلفوكساييد كبادئ ، وقد أجريت دراسة تفصيلية لخصائص محاليل المتضاعفات الناتجة ، وجد أن المتضاعف AIBN . PEZالمنفرد والمتضاعف المزدوج كلاهما يذوبان بسهولة في الماء وهذا يشير على السلوك الأليكتروليتي لـ سلوك اللزوجة للبولي الكتروليتات ، حيث تنخفض قيم اللزوجة الذاتية بزيادة القوة الأيونية PEZكذلك أظهر لمحاليلها المائية.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

1.1 Introduction

Water-soluble polymers are produced in large quantities, and are widely used in industry and consumer products. There are two major classes of water-soluble polymers; non-polyelectrolytes and polyelectrolytes. All water-soluble polymers share the common element of having hydrophilic polar functional groups that may be non-ionic, anionic or cationic. The anionic and cationic polymers together are referred to as polyelectrolytes, while the non-ionic ones are called non-polyelectrolyte. The major contributors to the nonpolyelectrolyte group of water-soluble polymers are poly(acrylamide), poly(acrylic acids), poly(vinyl alcohol), poly(ethylene oxides) and the naturally occurring water-soluble polysaccharides.

Cationic polyelectrolytes can be grouped into three categories; ammonium (primary, secondary, tertiary and quaternary), sulfonium and phosphonium compounds.

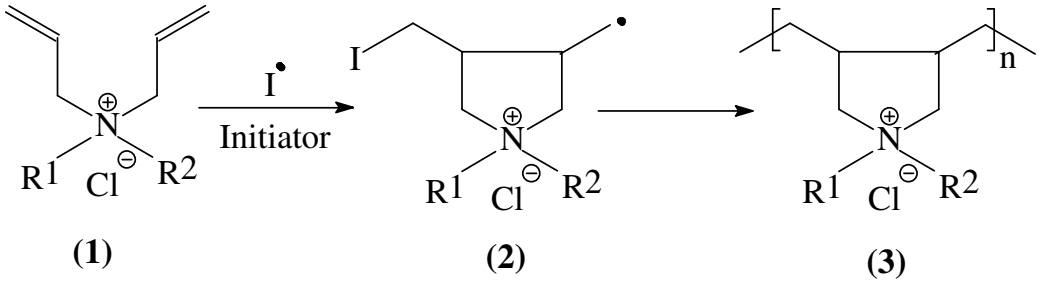
Of these, the ammonium-based polymers are the most extensively used in industry [1-3].

Phosphonium compounds have not been synthesized to high molecular weights, and sulfonium monomers are generally unstable and less readily available than quaternary ammonium monomers [4]. The quaternary ammonium functional group is highly hydrophilic lending high water solubility to the quaternary ammonium polyelectrolytes.

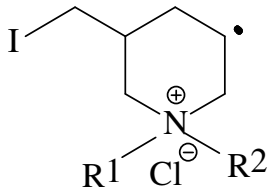
The cationic polyelectrolytes have found extensive industrial and commercial applications [5-10] as paper additives, as de-emulsifier of dispersed oil, in sludge dewatering, in sedimentation of suspended polymers, as paint thickeners, as flocculating agents, in enhanced oil recovery and coagulant aid in potable water, for electro conductivity in electropolarography and wastewater treatment.

Butler and coworkers have polymerized a large number of diallyl quaternary ammonium salts. Pioneering works of Butler and coworkers [11-14] led to the cyclopolymerization of a variety of diallyl quaternary ammonium salts **1** (scheme 1) to yield water-soluble homo- **3** and co-polymers **4**. The polymerization proceeds via alternating intra-inter-molecular chain propagation, termed cyclopolymerization, involving the kinetically preferred five-membered cyclic structure **2** [15] instead of thermodynamically stable six-membered ring **5.**

Poly(diallyldimethylammonium chloride) alone accounts for over 1000 patents and publications. The dialkyldiallylammonium salt- sulfur dioxide copolymers [16-19] are also manufactured commercially, and are useful as textile furnishes, polymer additives, coagulants and thickeners [16]. Cross-linked polysulfones are used as ion exchange beds. Tri- or tetraallylammonium salts have been used in removal of salinity from brackish water [20] and in the extraction of uranium [21].



(1) **(2)** **(3)**



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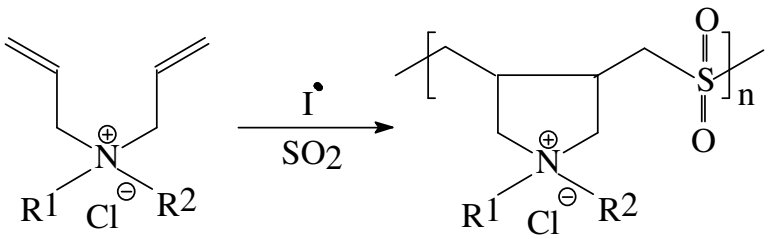
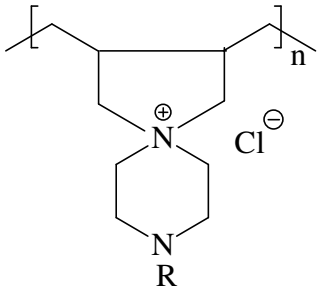


(1) **(4)**

Scheme 1

Modifications of Butler's monomers have provided entries [22-29] into the amphoteric polymers containing zwitterions on the same monomer (i.e, betaines) or along the same backbone (i.e, ampholytes). Amphoteric polymers have also found many applications in various fields [30,31] including their use as a simple model [32,33] for understanding the complex behavior of proteins. Amphoteric polymers, unlike polyelectrolytes, can exhibit "anti-polyelectrolyte" behavior [34-39] i.e, enhancement in viscosity and solubility in the presence of added electrolytes (e.g. NaCl) due to the neutralization of the ionically cross-linked network in a collapsed coil conformation of the polyampholytes.

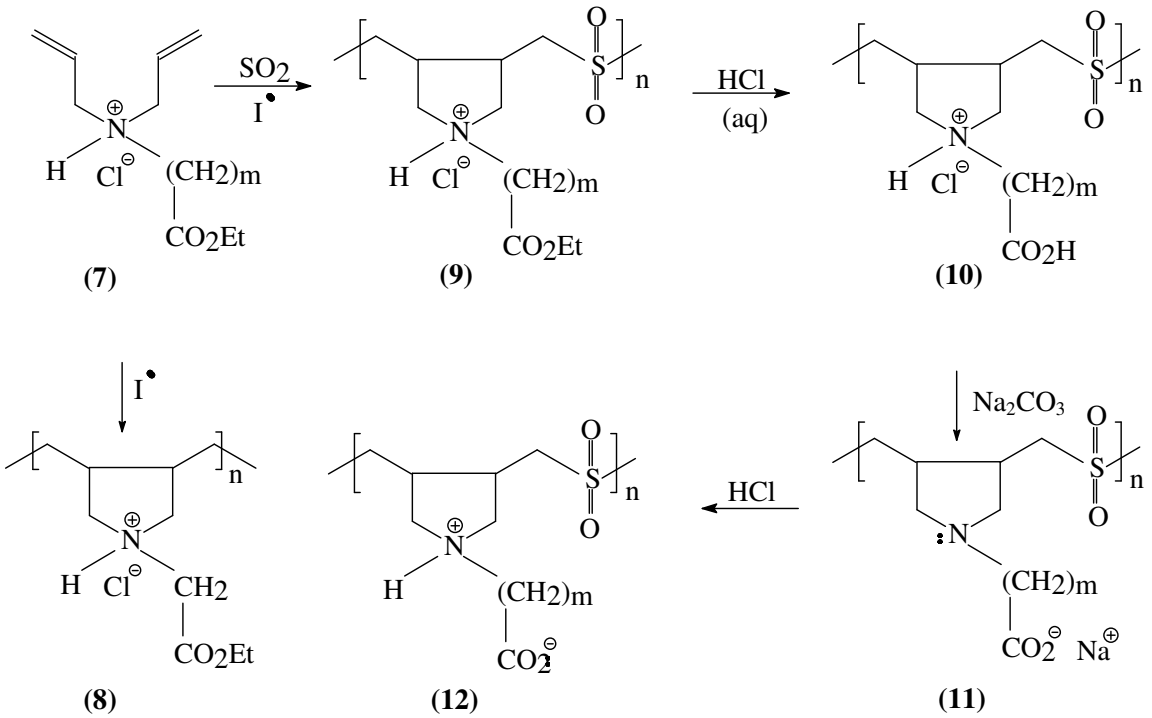
Hydrophobically associating copolymers of the monomeric salts **1** may have potential application in enhanced oil recovery (EOR) and other applications where viscofication of water is of interest [40,41]. Modified diallylammonium copolymers containing a few mole percent of a long chain alkyl (R) group have been shown to increase viscosity due to interchain association of the appended hydrophobic tails [42-44]. Further extensions into the area of water-soluble polymers have been reported [45-47] which describe the synthesis of a novel class of piperazine based homo-and co-polymers containing quaternary as well as trivalent nitrogen in the same polymer **6**.



where R = CHO
R = H

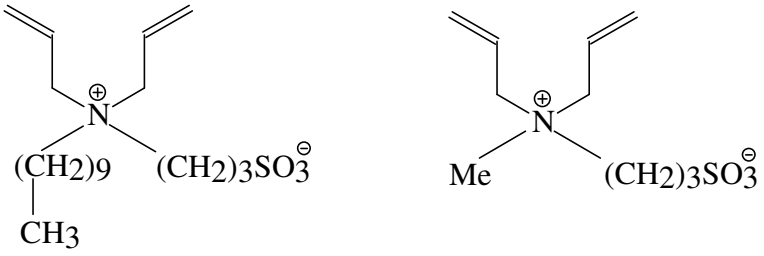
(6)

Quaternary ammonium salts having carboxy group in the pendant have been cyclopolymerized to polybetaines that show pH responsive solution behavior due to the incorporation of the pH-triggerable carboxybetaine functionality [25,27-29,48]. However, the use of amine salt **7** (instead of a quaternary salt) with a carboxy pendant permitted [49,50] the generatation of trivalent nitrogens in the resultant homo **8** and co-polymers **9** (Scheme 2). The cationic polyelectrolyte (CPE) **9** has been converted to the cationic acid salt (CAS) **10**, the anionic polyelectrolyte (APE) **11** and polybetaine (PB) **12.** The presence of strongly basic trivalent nitrogen as well as weakly basic carboxy functionalities has demonstrated [49-51] interesting pH-responsive solution behaviours in a wider spectrum of the pH scale. These polymers and poly(ethylene glycol) (PEG) have been used [49,50] to construct aqueous two-phase polymer systems, which may offer a friendly environment for the separation [52-55] of labile proteins.



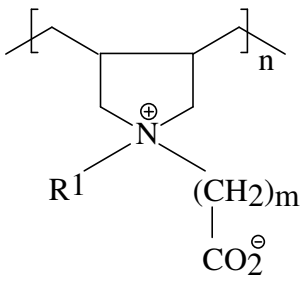
Scheme 2

There are only few reports [22,56] in the literature of polysulfobetaines (PSB) (polyzwitterions) derived from zwitterionic diallyl quaternary ammonium monomers e.g, **13, 14**.



(13) **(14)**

The development in the cyclopolymerization process has in recent years entered a new stage that deals with synthesis of pH-responsive ionic polymers. Quaternary ammonium salts-derived cyclopolymers **4, 15, 16** ($R^1 \neq H$) [22,24-26,35] with an anionic pendant show pH responsive solution behavior due to the incorporation of the pH-triggerable betaine functionality. However, the use of amine salt-derived polymers **4** (scheme 1) and **15** ($R^1 = H$) permitted the generation of two pH-responsive groups (a trivalent nitrogen as well as a carboxy) in the resultant polymer [36-38]. The presence of strongly basic trivalent nitrogen as well as weakly basic carboxy functionalities has indeed demonstrated interesting pH-responsive solution behavior in a wider spectrum of the pH scale. One of the most gratifying aspect of the polymer **4** ($R^1 = H$; $R^2 = CH_2CO_2^-$) is its almost zero solubility [36] in water below pH ~7 in presence or absence of salt thus, making it a suitable candidate [39] for applications in protein purification in two-phase aqueous polymer systems [40] since it will permit its effective removal from solution by precipitation.



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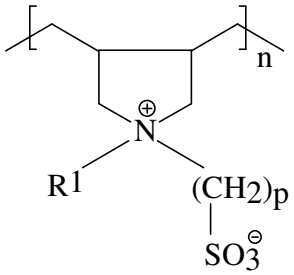


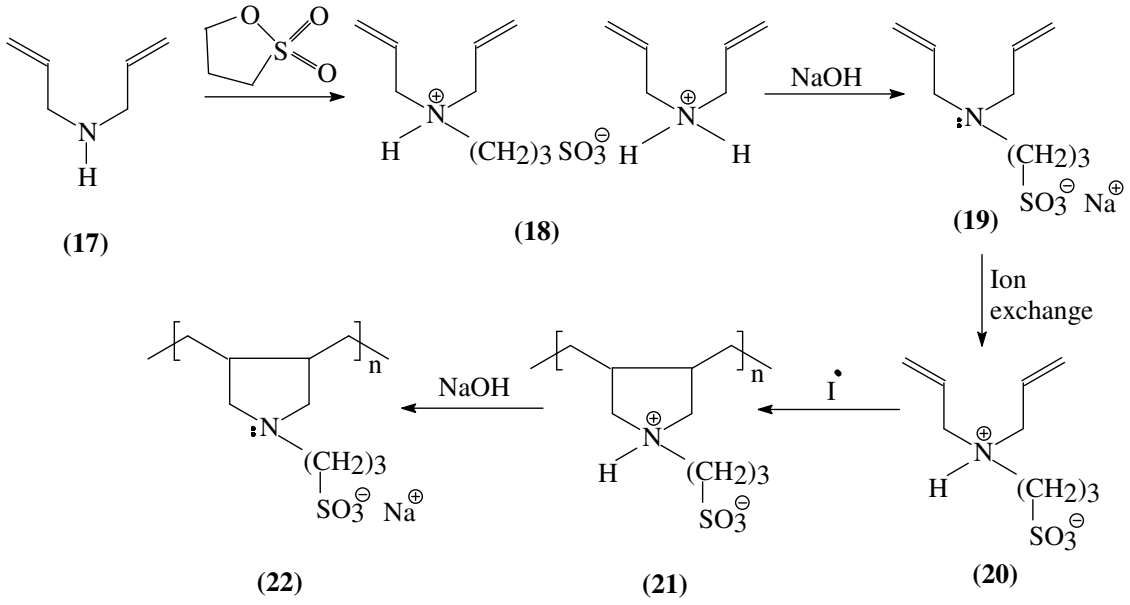
(16)

1.2 Aim of the work

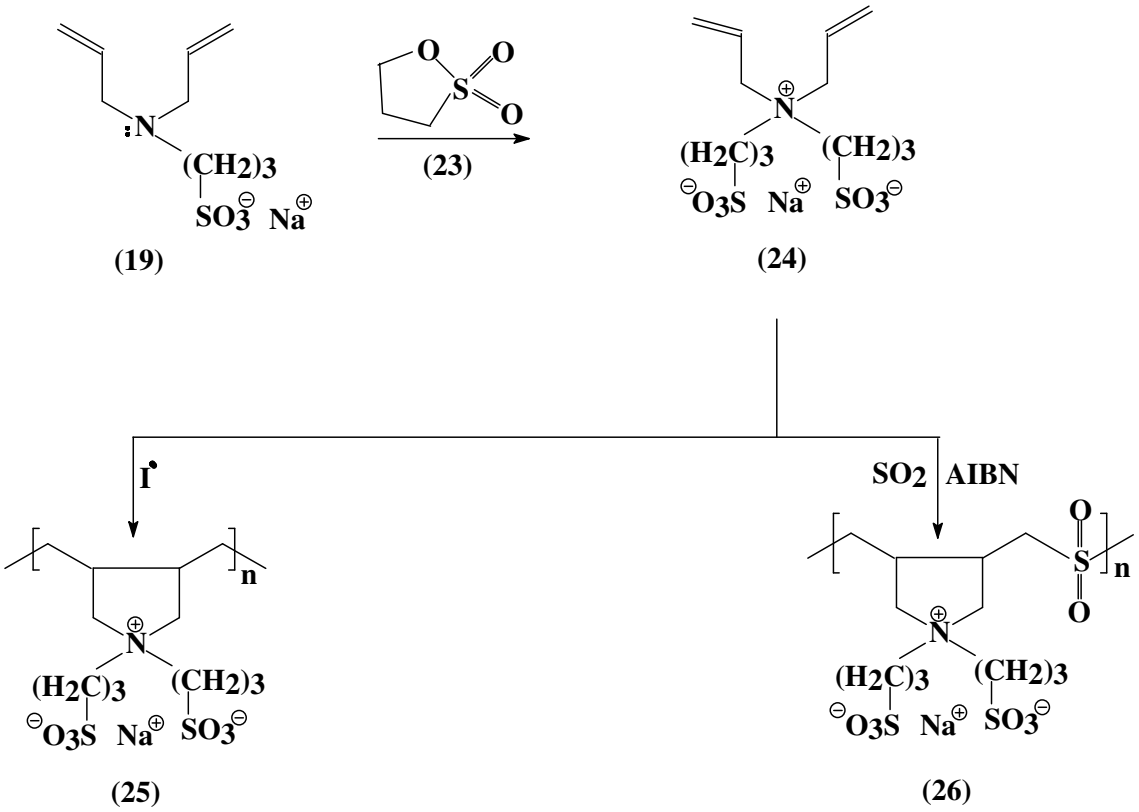
Viscosity curves for the poly(quaternary ammonium salts) are typically of polyelectrolytes in general, and unlike the behavior of nonionic polymers. Reduced viscosity increases with dilution thus resulting in very large intrinsic viscosities. This is attributed to increase in hydrodynamic volume of the polymers in dilute solution where large repulsive forces between positively charged nitrogen leads to the expansion of the polymeric backbone. The viscosity of polyelectrolytes in presence of strong electrolytes such as NaCl behaves like normal polymers, and the added salts decrease the viscosity of the polyelectrolytes tremendously. The polyampholytes (polyzwitterions), on the other hand, display opposite effect (which is called antipolyelectrolytic effects) in the presence of added salts; the addition of NaCl increases the viscosity of the polymer solution. In most cases polyampholytes are insoluble in water. Osmotic force, which tends to draw solvent into the polymer, is not of sufficient strength to rupture the three-dimensional network of intra and inter-chain ionic interactions. However, in the presence of added salt (e.g,. NaC1) the mobile ions are able to neutralize a portion of the ionic cross-links, thus resulting in the dissolution of the polyampholyte.

The **objective** of this research is

(I) To synthesize the diallylamine zwitterionic monomer [3-(*N, N* –diallylamino) propanesulfonate] **20** and electrolyte zwitterionic monomer [sodium 3-(*N, N* –diallylamino) dipropanesulfonate] **24** from the widely available starting material diallylamine **17** as shown in schemes 3 and 4.



Scheme 3



Scheme 4

(II) To homopolymerize the zwitterionic monomer **20** to the polysulfobetaine **21** and anionic polyelectrolyte **22.**

(III) To homopolymerize and copolymerize the electrolytic zwitterionic monomer **24** to give poly(sulfobetaine – sulfonate) **25** and poly(sulfobetaine - sulfonate)-co-sulfur dioxide **26**.

(IV) To study in detail the solution properties of the polymers **21, 22, 25** and **26.**

(V) To determine the basicity constant of the protonation of polymer **22** and its use in the constitution of aqueous two-phase polymer system with polyethylene glycol (PEG).

1.3 Work Methodology:

The monomers **20** (zwitterionic monomer) and **24** (electrolytic - zwitterionic monomer) would be subjected to polymerization reactions using different radical initiators in different solvents at different temperatures in order to optimize the yield of the polymers **21** and **25** (shown in schemes 3 and 4) and their solution properties. In our endeavor to synthesize special polymers containing pH-triggerable functionality (*N*) that are expected to exhibit pH responsive solution behavior, the polymer **21** would be converted to the anionic polymer **22** on treatment with sodium hydroxide.

The zwitterionic monomer **20** will be treated with sodium hydroxide to give the anionic monomer **23**, which on reaction with 1,3-propane sultone is expected to give the special monomer **24** containing the zwitterionic and electrolytic functionalities on the same monomer (Scheme 4).

The copolymerization of the electrolytic-zwitterionic monomer **24** with sulfur dioxide in dimethyl sulfoxide using azo-bis-isobutyronitrile (AIBN) would also be studied (scheme 4) to synthesize copolymer **26**.

The copolymerization reaction conditions will be optimized and solution properties of the copolymer **26** will be investigated.

It would be interesting to investigate the solubility behaviour of these polymers **21, 22, 25** and **26** in aqueous medium. Zwitterionic polymers (known as polybetaines) are insoluble in water and can be solubilised by addition of strong electrolytes such as sodium chloride. This is because the added electrolyte ions break the strong inter-chain associations occurring in polybetaines. It will be interesting to investigate whether the presence of electrolytic ion pair in zwitterionic polymers will **25** and **26** impart water solubility in the absence of added electrolyte.

Furthermore, polybetaines exhibit increasing intrinsic viscosity in solutions of higher salt concentrations. This is referred to as anti-polyelectrolyte effect. Polyelectrolytes, as is well known, exhibit decreasing intrinsic viscosity with increasing salt concentration. The presence of both the electrolytic and zwitterionic functionalities may impart interesting viscosity behaviour in these polymers.

In our endeavor to synthesize special polymers containing pH- triggerable functionality (N) that are expected to exhibit pH responsive solution behavior, we have directed our attention to cyclopolymerize the diallylamine salts **20** and **24** (scheme 3 and 4). To the best of our knowledge the polymers based on amine salt of the type **20** and **24** containing sulfobetaine moiety have not been reported to date. In fact the polymer based on diallyl quaternary ammonium salt **24** containing zwitterionic as well as electrolytic sulfobetaine moieties on the same monomer will indeed represent the synthesis of a novel class of polymers with tremendous theoretical and practical significance. The anticipated polymers **21, 22** and **25** will indeed provide a unique opportunity to study the solution

behavior of these interesting classes of polymers. The study would also provide an opportunity to compare the viscosity behaviour of the PSB **21** and its corresponding APE **22** having similar degree of polymerization.

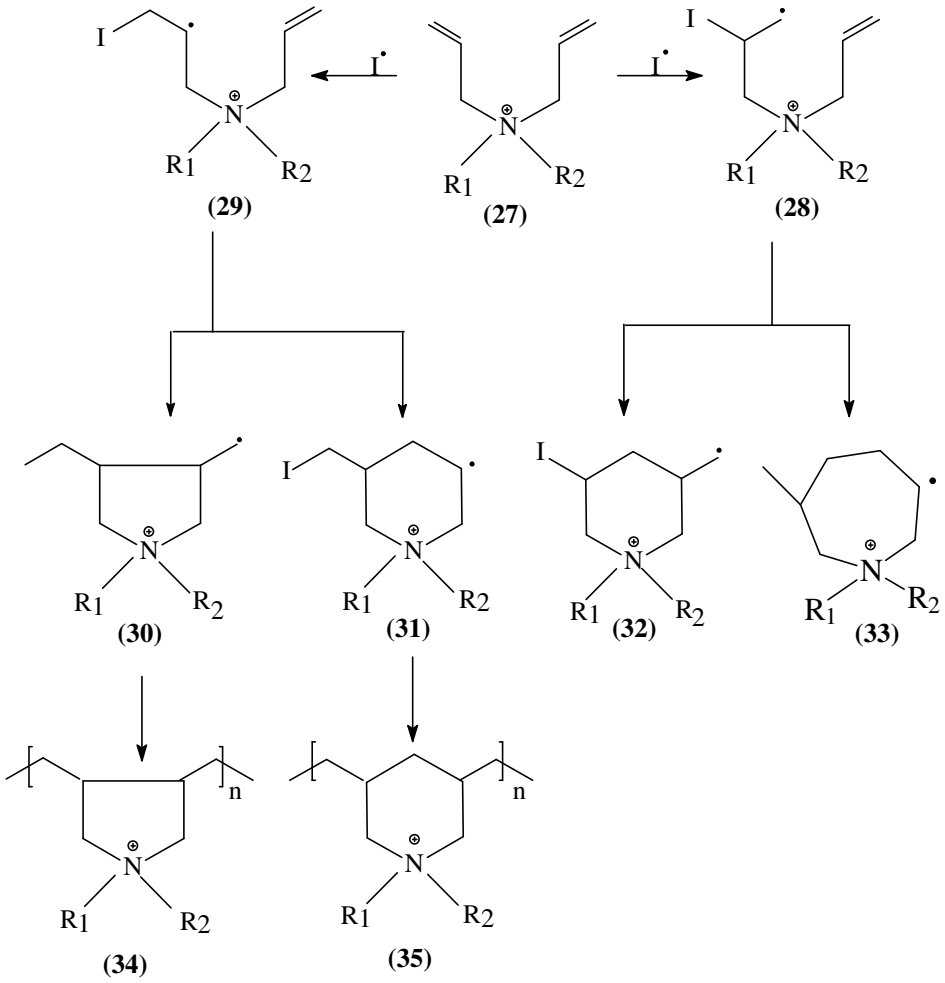
CHAPTER 2

HISTORICAL DEVELOPMENT

2.1 History of Polymerization of Diallyl Amines

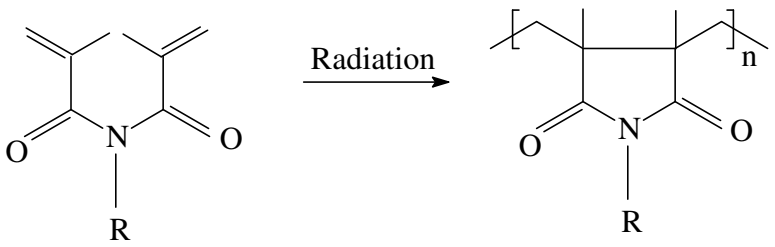
Diallylamines belong to the broad class of non-conjugated dienes. In the early 1930's Staudinger [56] proposed that non-conjugated dienes lead to cross-linked, hence insoluble, nonlinear polymers or copolymers. In 1949, Butler & Bunch [10,57] polymerized tri and tetra allyl quaternary ammonium salts to form highly cross-linked water insoluble polymers. The first instance of an exception to Staudinger's proposal was reported in 1951, when Butler and Ingley [12] polymerized diallyl quaternary bromide salts to yield water-soluble linear polymers. Early investigation involving degradation studies [58] revealed that the polymer possesses cyclic structures. Flory [59] proposed a six membered structure for radical initiated cyclopolymerization of 1,6-dienes (symmetrical or unsymmetrical) where predominance of more stable intervening radicals controls vinyl polymerization.

Scheme 5 shows the possible ring structures in cyclopolymerization of diallylamines. It has now been shown that the cyclopolymerization of diallyl quaternary ammonium salts **27** leads to five membered cyclic structure **34** via the less stable intermediate **30** under conditions of Kinetic Control [60]. The formation of this structure by the reaction sequence **27→29→30→34** corresponds to a head to head polymerization process.



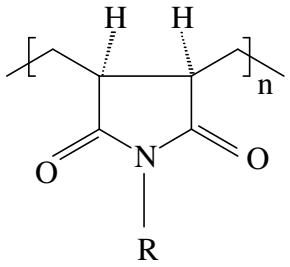
Scheme 5

Predominant or exclusive formation of five membered ring is observed in the radiation induced cyclopolymerization of *N*-substituted dimethacrylamides [61-63] **36** in the liquid, super liquid and crystalline states.



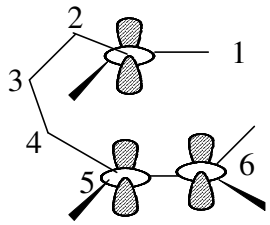
(36)

Five membered rings are also obtained by copolymerization of certain diallylamines and quaternary ammonium salts [64] which corresponds to a head to head polymerization process. However, when the allyl groups are substituted in the position 2, mixture of both five and six membered rings were formed. The polymer **37** has been shown [6] by ^{13}C NMR study to consist predominantly of five membered ring linked largely in a 3,4 – cis configuration.



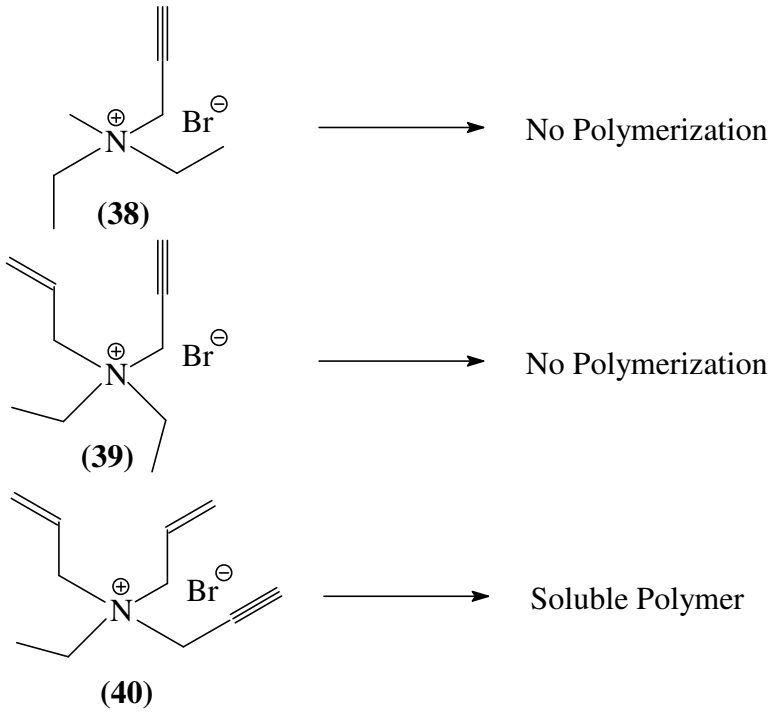
(37)

Most non-conjugated dienes appear to undergo cyclopolymerization involving an intramolecular ring-closing mechanism rather than polymerization through a single allyl group, which would lead to cross-linking or other mode of propagation [2]. The preference for cyclization has been attributed to a smaller decrease in entropy relative to intermolecular addition. The kinetic control of the intermolecular cyclization reaction is explained in terms of stereoelectronic requirements of the transition state [65]. Maximum overlap of half filled p-orbital with the vacant $\prod^*$ orbital of the double bond demands the approach of the radical along a vertical line from one of the carbon atoms of the double bond with the orbital holding the three electrons in the same plane throughout the reaction. This requirement is met in the 1, 5 cyclization but not in the 1,6 cyclization.



However, introducing bulky 5 substituents leads to increasing preference for the six membered ring structures.

Polymerization studies of unsaturated quaternary ammonium compounds containing propargyl substituents showed that only those compounds containing two or more allyl groups **40, 42** produced polymer and that the propargyl groups did not enter into the polymerization process. The unsaturated quaternary ammonium bromide **43** yields [66] water soluble polymer, from those compounds containing only two allyl groups in addition to the β-vinyloxyethyl group and water insoluble crosslinked polymers from those compounds having three allyl groups in addition to a β- vinyloxyethyl group. It was found that the β-vinyloxyethyl group did not enter into the polymerization under the conditions used.



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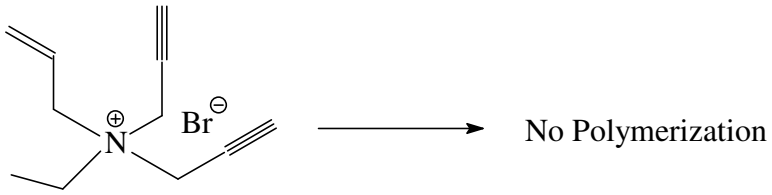

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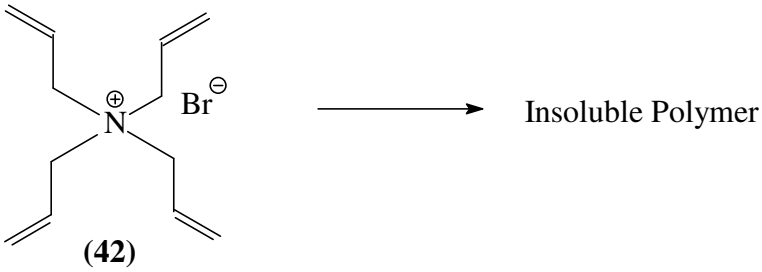

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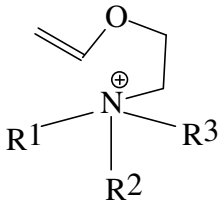
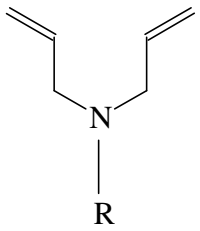


(43)

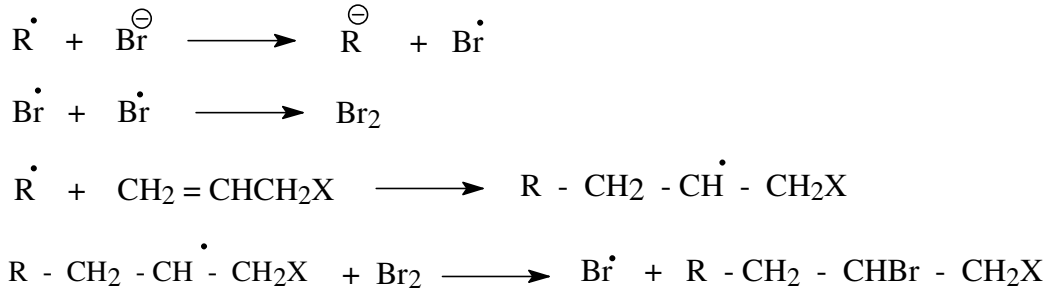
Generally, diallyl amines do not undergo free radical polymerization readily, but the protonated or quaternary salts do polymerize. The presence of electrophilic *N*-substituents in diallyl amines **44** activates the monomers towards radical attack [67].



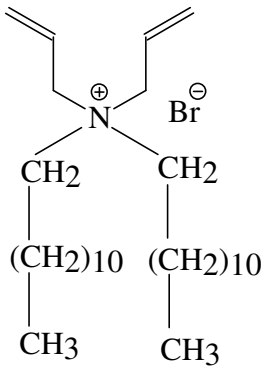
(R = CN, COR', SO_2R' etc)

(44)

It is known that allyl compounds do not yield high molecular weight polymers due to depropagation and chain transfer reactions involving hydrogen abstraction from allylic position. Polymers of diallyl quaternary ammonium chlorides have higher molecular weights (and are therefore more useful) than the polymers of diallyl quaternary ammonium bromides [68]. Initiator radicals probably oxidize the bromide ion more easily to bromine, which then inhibits polymerization by consumption of initiator radicals, and by termination of propagating chains.

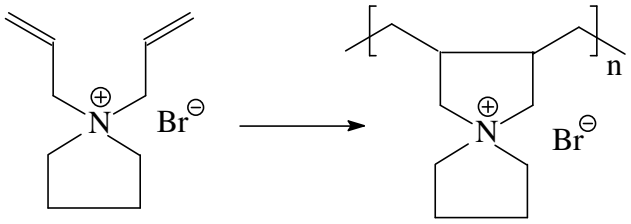


Diallyl quaternary ammonium bromide **45** is a vesicle forming monomer. The double tail lipophilic portion of **45** makes it capable of forming vesicles in water. Polymerization of **45** by gamma ray irradiation yields the polymeric counterpart. It has been shown that the polymerized vesicles retain the structure of the monomeric vesicles and simultaneously exhibit higher stability [69].



(45)

N, N-diallyl pyrrolonidiniun bromide (DAPB) **46** has been polymerized to poly-DAPB **47** by free radical polymerization. That the polymerization proceeds by cyclopolymerization leading to the five-membered ring structure was confirmed by comparison of ^{13}C NMR spectra of poly-DAPB with those of model compounds [70].



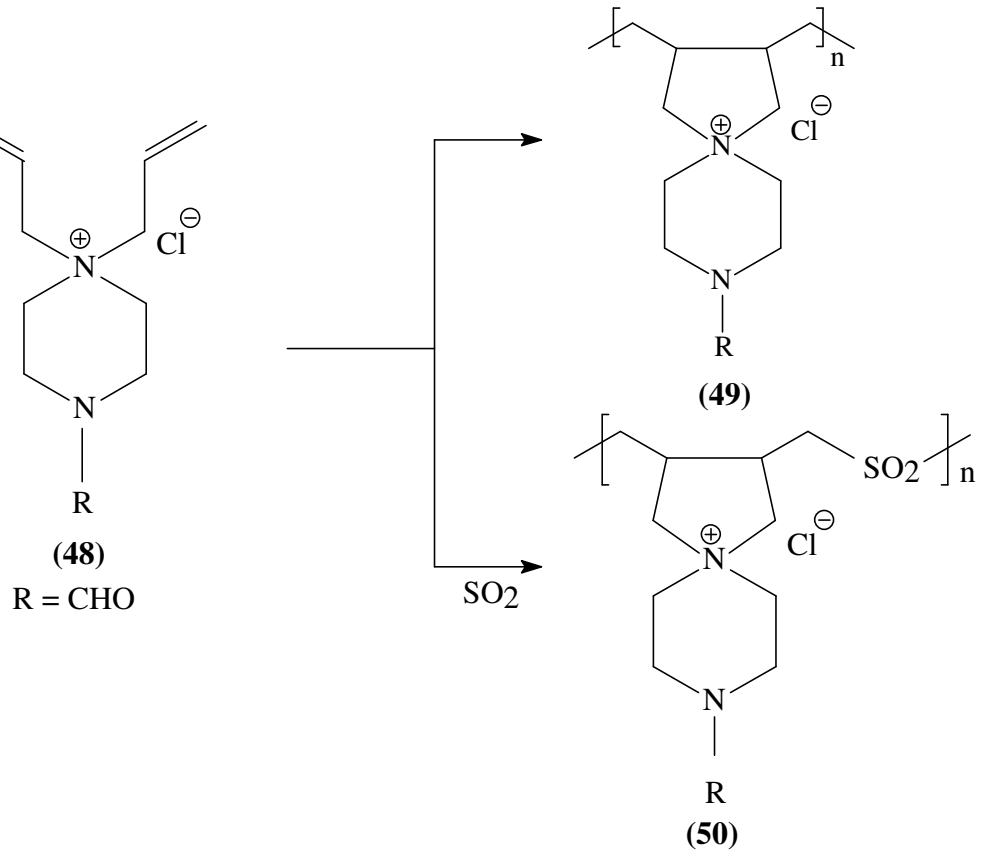
DAPB

Poly DAPB

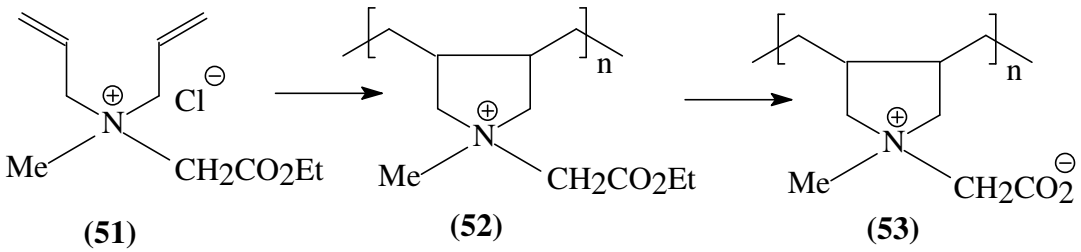
(46)

(47)

N, N-diallyl-4-formylpiperazinium chloride **48** was polymerized using tertiary butylhydroperoxide initiator. The aqueous two-phase system of the homopolymer **49** and copolymer (with SO_2) **50** was studied [18].



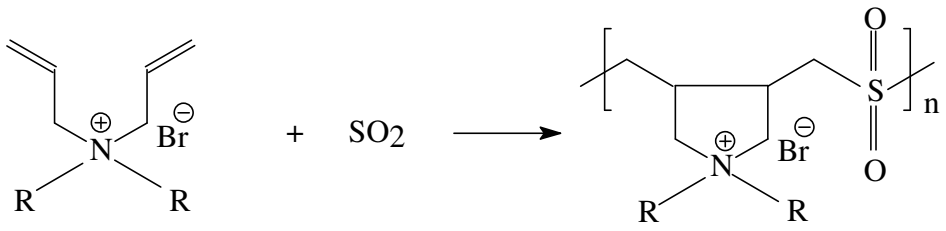
Polymerization of **51** using ammonium persulphate (APS) initiator to polyelectrolyte **52** (which was hydrolyzed to the zwitterionic polymer **53**) has been reported recently [28]. It has been shown that **53** exhibits antipolyelectrolyte viscosity behavior like most zwitterionic polymers.



2.2 Copolymerization in non-conjugated dienes.

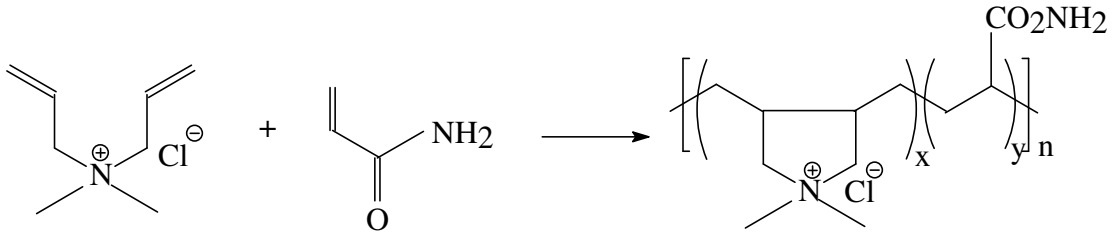
`

Alternating copolymers **55** are obtained on cyclopolymerization of diallyl compounds **54** with sulfur dioxide [19,71] in different solvents with free radical initiators such as ammonium persulfate, azobisisobutyronitrile, *t*-butylhydroperoxide, and dilauroyl peroxide.



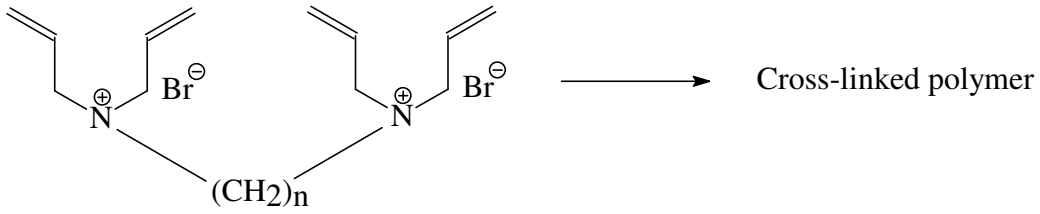
(54) **(55)**

It is reported [72] that dimethyldiallylammonium chloride **56** undergoes copolymerization with acrylamide to give the polymer **57**.



(56) **(57)**

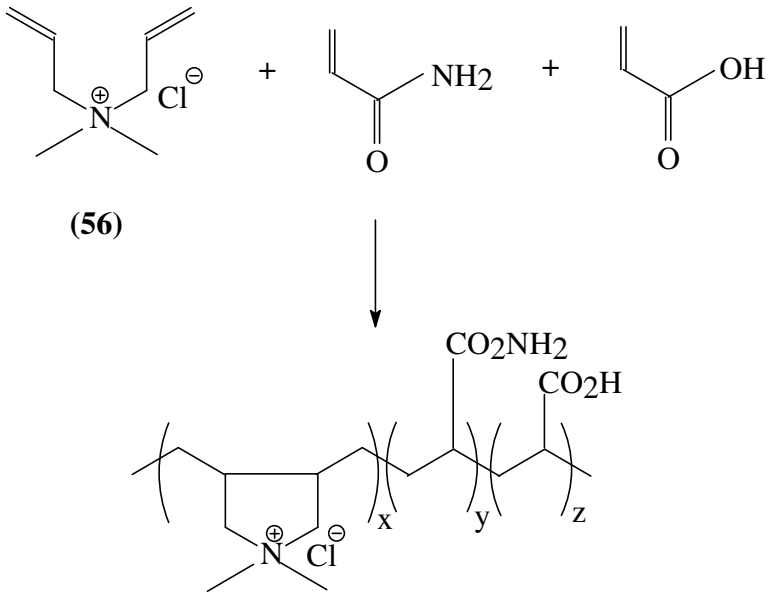
Ion exchange resins were obtained by the polymerization of the tetraallyl derivatives **58** of 1,n- diaminoalkanes [73-75]



(58)

Amphiphilic cyclopolymerization [41] of diallyldimethylammonium chloride and diallyl alkyloxybenzyl methylammonium chloride was studied by free radical polymerization in aqueous solution. It was observed that addition of sodium dodecyl sulfate (SDS), below the critical micelle concentration, to the copolymer solution results in a large increase in the viscosity of the polyelectrolyte.

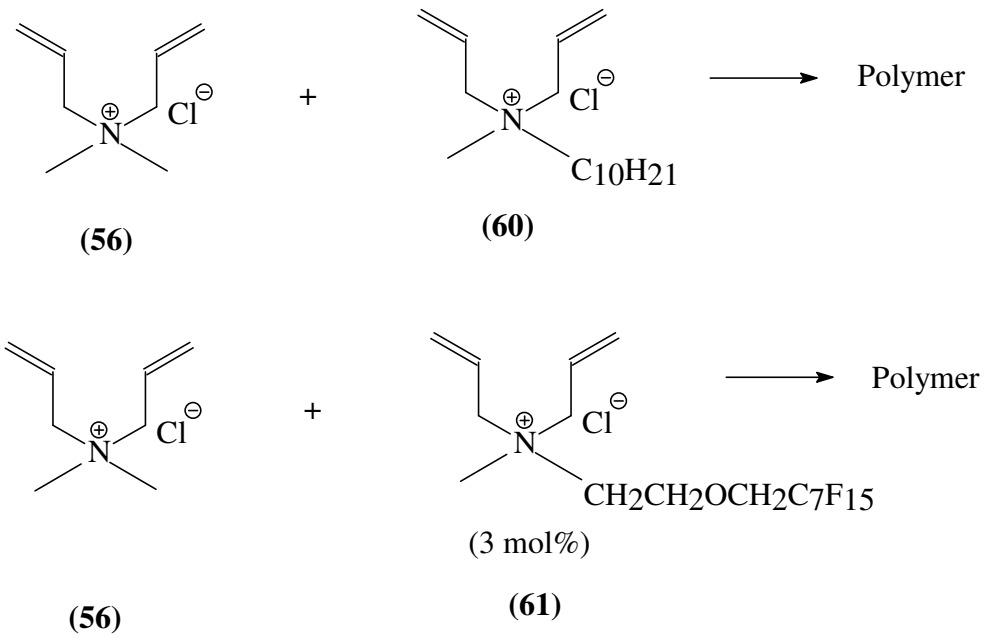
Polyelectrolytes have also been synthesized by terpolymerizing dimethyldiallylammonium chloride with acryl amide and acrylic acid. These polymers, **59,** are used as dry strength resins in paper manufacturing [76].



(56)

(59)

Hydrophobically associating ionic copolymers [40,41] of diallyl dimethyl ammonium chloride **56** with 1 to 4 mol% of diallyldecylmethylammonium chloride **60** and methyldiallyl (1,1 dihydropentadecafluorooctaoxyethyl)- ammonium chloride **61** are synthesized and the copolymer exhibited significant increases in the viscosity compared to poly(diallyldimethylammonium chloride).



A review and use analysis of poly(diallyldimethylammonium halide) has been published [3]. A variety of commercial products have been developed using cyclopolymerization of these quaternary salts. Poly(diallyldimethylammonium chloride) is the first polymer in this series to be manufactured by a number of suppliers. It possesses optimum functional properties for application to electrographic paper reduction processes [1]. This polymer has also found application as paper additives. It is used in water treatment as a flocculant. In the industry, this polymer has found application as a coagulant in the coal floatation process. It is used as a de-emulsifier of dispersed oils in the cosmetic field, as a biocide in water, and as a detergent additive.

The copolymers of these quaternary salts with sulfur dioxide [19] have similar industrial uses. Tetraallyl diammoniumdichloride salts give ion-exchangers of both superior rate and capacity for use in extraction of uranium [21]. Polytriallylamine [77] is

reported to be a thermally regenerated ion exchange resin [20] for the cheap removal of salinity from brackish water. Diallylamine hydrochloride with a suitable cross linker is reported to give a polymer used as a super anion exchanger. Cyclopolymerizaton of suitable salts have also resulted in the formation of strongly basic ion exchange resins [73,75]. The hydrophobically associating copolymers may have potential application in enhanced oil recovery and other applications where viscosification of water is of interest.

Polyelectrolytes are generally prepared by free radical (homo- and co-) polymerization of an ionic monomer or neutral monomer. In the latter case, the subsequent reaction on the preformed neutral polymer leads to ionic polymers. However, the first case offers greater advantage in controlling over the structure and properties of the final polyelectrolyte. The second case is more difficult to control as the amount of charge becomes greater and greater during conversion of a neutral polymer to one of high charge density, and as such most reactions rarely go to completion.

There has been considerable academic and industrial interest in the preparation of new ionic polymers [76,78]. These studies included the area of cationic and anionic polyelectrolytes, since both classes have unique chemical and physical properties.

2.3 Polyampholytes

Ampholytic (zwitterionic) polymers are either formed from polymerization of inner salt (zwitterionic) monomer or from the preformed neutral polymer.

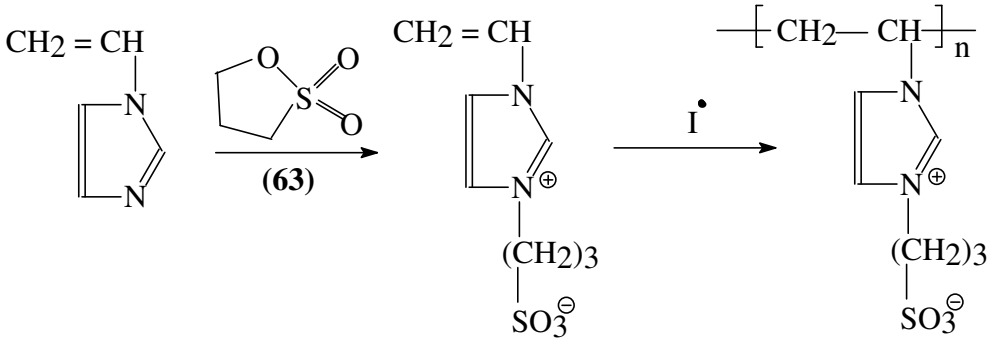
The polyampholytes show unusual properties in aqueous solution [79,80]. The polymers are insoluble in water and have hydrogel characteristics. However, the polymers could be dissolved in certain aqueous salt solutions. The solution properties are found to depend on the type and concentration of the salt added. In contrast to polyelectrolytes, the reduced viscosities of polyamphoytes increases with increased salt concentration. The greater the site binding ability of either the cation or anion, the greater the reduced viscosity [80].

For the solubilizaton of polyampholytes by aqueous salt solution, the cations and anions of low molecular weight electrolytes could be considered to enter ionically cross-linked network of the polymer through osmotic forces [35]. These forces cause the polymer to swell when placed in water. The insolubility of plyampholytes in water is attributed to the fact that osmotic forces that tend to draw solvent into the polymer are not sufficient to rupture the ionic crosslinks. Polyampholytes swell until elastic forces of the network balance the osmotic forces. In the presence of added salt (NaCl) the solvent (H_2O) along with the mobile ions is drawn into the polymer, and the polymer swells as usual. However the mobile ions of the added salt neutralize a portion of the ionic

crosslinks resulting in the continual decrease of the elastic forces, which tend to oppose the continued swelling, as a result polymer swells until the gel finally dissolves.

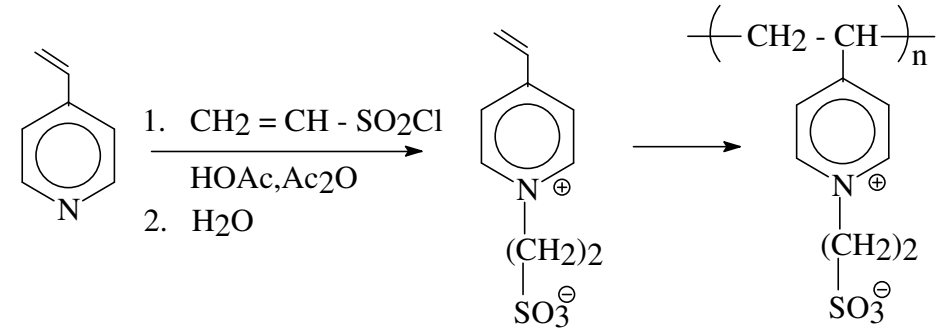
One of the major drawbacks of the use of high molecular weight polyelectrolytes in enhanced oil recovery (EOR) is the drastic decrease of the viscosity of their aqueous solutions in presence of salt (NaCl, *etc*) [81]. However zwitterionic polymers show "antipolyelectrolyte behavior"[37] and have low or no solubility in water but greatly enhanced solubility and extensive chain expansion, hence viscosification, upon increasing salt concentration.

Quaternarization of *N* vinylimidazole **62** with propanesultone **63** gives inner salt **64**, which on free radical polymerization yielded the polyzwitterionic homopolymer **65** [35].

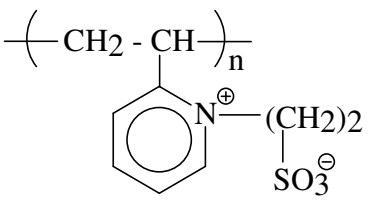


(62) **(64)** **(65)**

A disadvantage in all reported synthesis of poly(vinyl sulphobetaines) is that only propane- and butane- sultones are known to yield ampholytic monomer. In order to circumvent the problem, the following monomer **67** was synthesized using alkenylsulfonylchlorides [34].



(66) **(67)** **(68)**



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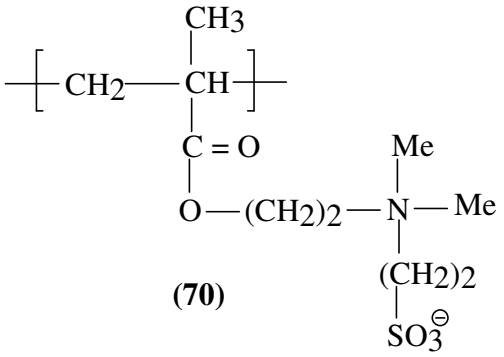

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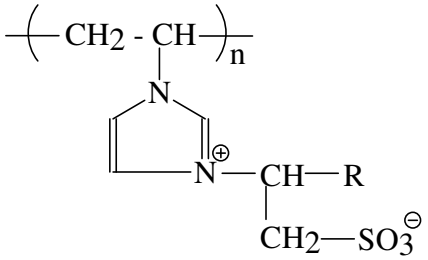
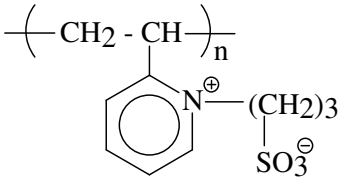


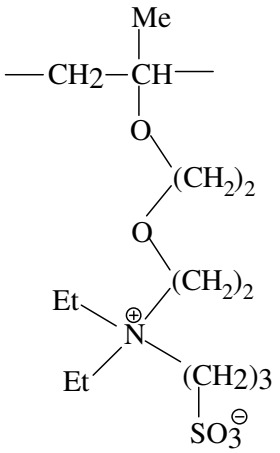
(**71**) R = H
(**72**) R = Me

The monomer, on free radical polymerization afforded the polysulfobetaines **68**. Likewise, the polysulfobetaines **69-72** were synthesized. As anticipated, the polysulfobetaines **68-71** are insoluble in water but readily dissolves in aqueous NaCl. Such behavior has been interpreted [37,82] by assuming the presence of a collapsed coil in water due to intrasalt and intrachain interactions. Such interactions are broken up in the presence of added low molecular weight electrolytes. While the polysulfobetaine **71** was found to be insoluble; the polymer **72** readily dissolves in water. The presence of bulky groups near the quaternary center diminishes the effectiveness of the intrasalt and intrachain interactions. Structural modifications thus affect the delicate balance between intramolecular interaction and hydration. The temperature and molecular weight have also been shown to govern the solubility of polyampholytes [37].

Upto 1987 only two other poly sulphobutaines **73** and **74** were known [36] to be soluble in water. Their solubility was again attributed to the presence of bulky groups near the quaternary nitrogen center.

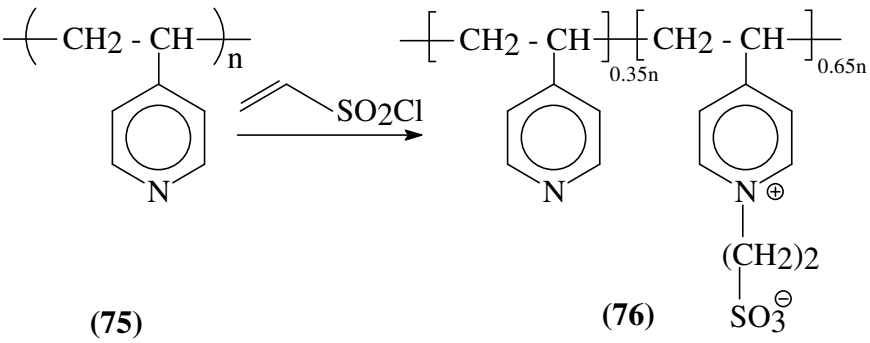


(73)



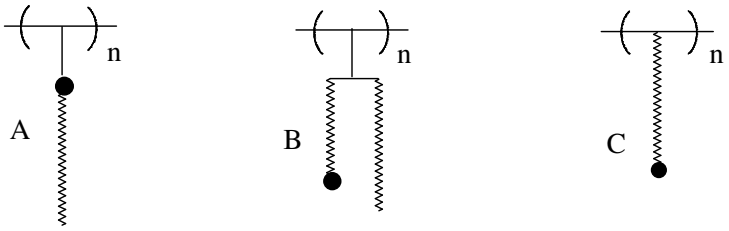
(74)

Attempts [34] to quaternize the polymer **75** were accomplished only to the extent of 65%.



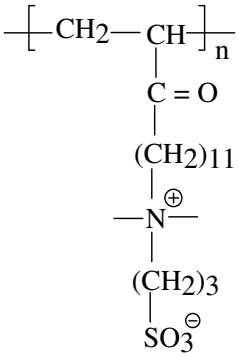
(75) **(76)**

Synthesis and bulk properties of several polyzwitterionic surfactants have been reported [22,83]. The solubility of these polymers is correlated with their molecular geometry. Molecular architecture of polyampholytic surfactants (poly soaps) envisages three main types of structures. In structure **77** the charge centers remain close to the polymeric backbone and is called “head-attached” type. Structure **78** represents polyampholyte of the “mid tail- attached” type. The structure **79** represents polymers of the “tail – end” type where the hydrophobic tail is attached to the backbone. Polymer **80** (“tail end- attached” type) is found to be soluble in fomamide and water but insoluble in ethanol. The polymer **81** (“mid tail- attached” type) is soluble in formamide but insoluble in water and ethanol.

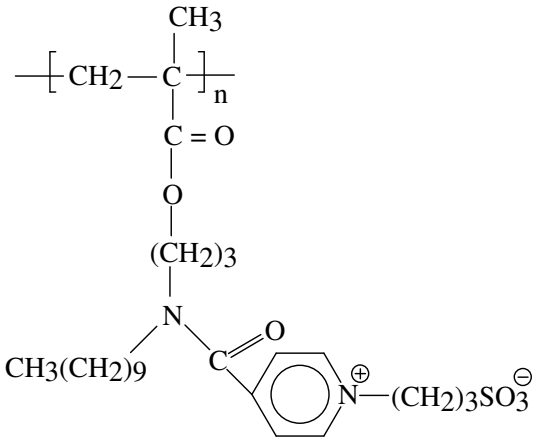


Back bone "head-attached" Back bone " mid tail-attached" Back bone "tail end-attached"

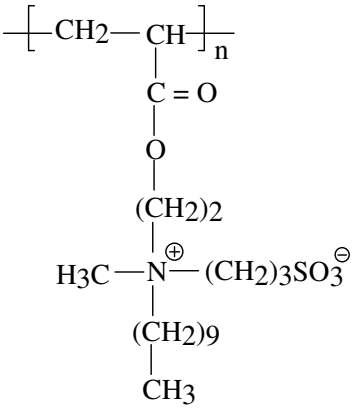
(77) **(78)** **(79)**



(**80**)



(81)

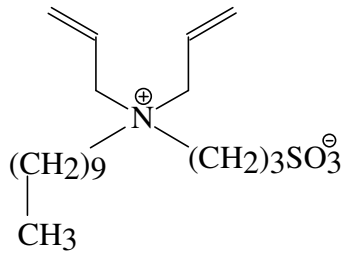


(**82**)

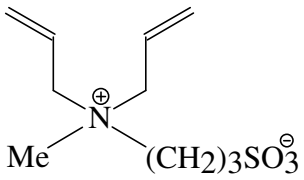
The polymer **82** ("head- attached type"), however, is found to be insoluble in water and formamide but soluble in ethanol. The tail end attached type polymer as represented by **80** is found to be soluble in water. It was noted that the solubility of these polymers in water is improved by adding salt as expected.

Obviously, the "skin" of the polymers exposed to the solvent mainly controls the solubility characteristics. Thus ionic/zwitterionic "skins" require polar solvents, and hydrocarbon skins require less polar solvents. In agreement with this, polymer **81**, which represents the mid- tail attached type, exhibits intermediate solubility behavior. These fully zwitterionic polymeric surfactants represent an unconventional but interesting type of micellar polymers (polysoaps). They combine advantageously the behavior of ionic and non - ionic poly soaps.

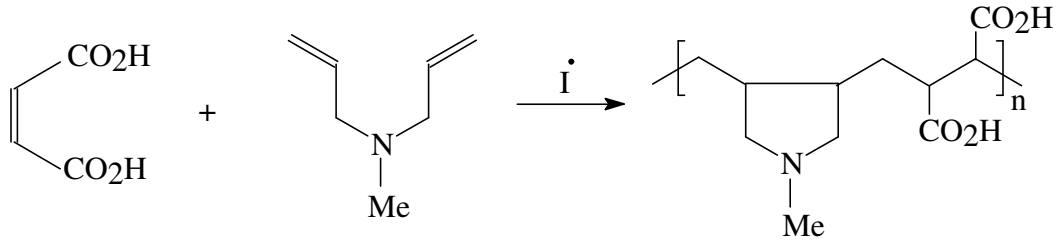
There are a few references in literature of polyampholytes derived from *N, N* – diallyl quaternary ammonium monomers. Zwitterionic polysoaps are prepared by radical homo-polymerization of the monomer **83**.



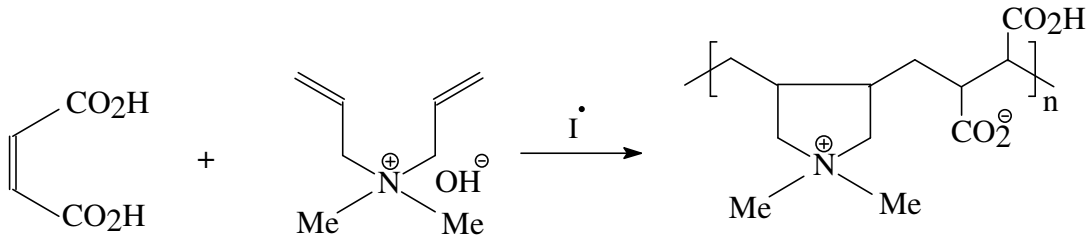
(83)



(84)



(85)



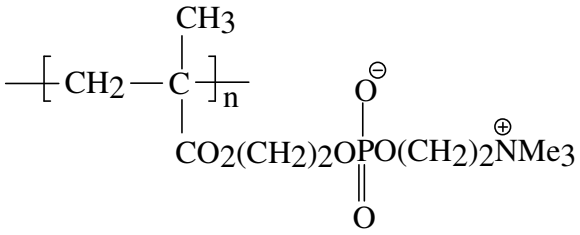
(86)

While the homo-polymer of the sulfobetaine **84** has been reported in the literature [34], the solution properties of this polysulfobetaine have not been described.

Alternating ampholytic copolymers of maleic acid with allylamine, diallylamine, methyldiallylamine and diallyl quaternary ammonium salt were synthesized by free radical polymerization [84] (to give, for example, the copolymers **85, 86** *etc*). The copolymers are characterized by viscometry, potentiometry and turbidimetry, and their properties are found to depend on pH and ionic strength of the aqueous solutions of the polymers. The influence of the cationic units on solution properties of the

polyampholytes is discussed from the aspect of zwitterions formation. It was found that the viscosity of the polymers (e.g, **86**) decreases with increasing concentration of added NaCl; a marked contrast to the behavior observed in case of usual polyampholytes.

Ionic strength (I), and pH dependence of the intrinsic viscosity ([η]) of betaine-type polyzwitterions **87** have been investigated recently [85].



(87)

The linear relationship between $1/\sqrt{I}$ and [η] for ordinary polyelectrolyte was also observed for the polyampholyte **87** at low ionic strength near the isoionic pH (3.35) and over a wide range of ionic strength at other pH at high ionic strength and at pH 4, a reverse tendency is observed i.e, viscosity increases with increasing ionic strength. This suggests the release of attractive interactions between different charges with the increase of ionic strength. The polyampholyte behaves as a polyelectrolyte when positive charges are excessively populated in the molecule (pH = 1.0) and also even when a slight amount of net charges exists in the molecule as long as the magnitude of ionic strength is sufficiently low. Near isoelectric point, where the net charge in the molecule reduces to zero, the intermolecular attraction between oppositely charged groups on the chain is expected to make the polyampholyte coil tightly [86,87] in salt free condition and to be

expanded with increasing ionic strength .The drag reduction efficiency of several well characterized water- soluble polyampholytes has been studied [30]. Polyampholytes can reduce the energy loss due to friction in turbulent flow. A polymer molecule interacts with vortices that are formed in turbulent flow and dissipate energy necessary for the vortices to grow and thus reduces turbulence.

Polyampholytes have found applications [31] in biosensors and in amphoteric buffer for electrophoresis. Polyampholytes can also serve as a simple model [32,33] for understanding the complex behavior of random copolymer such as proteins. Preparation of novel biodegradable polyampholyte from partially dicarboxylated chitosan has been reported [88].

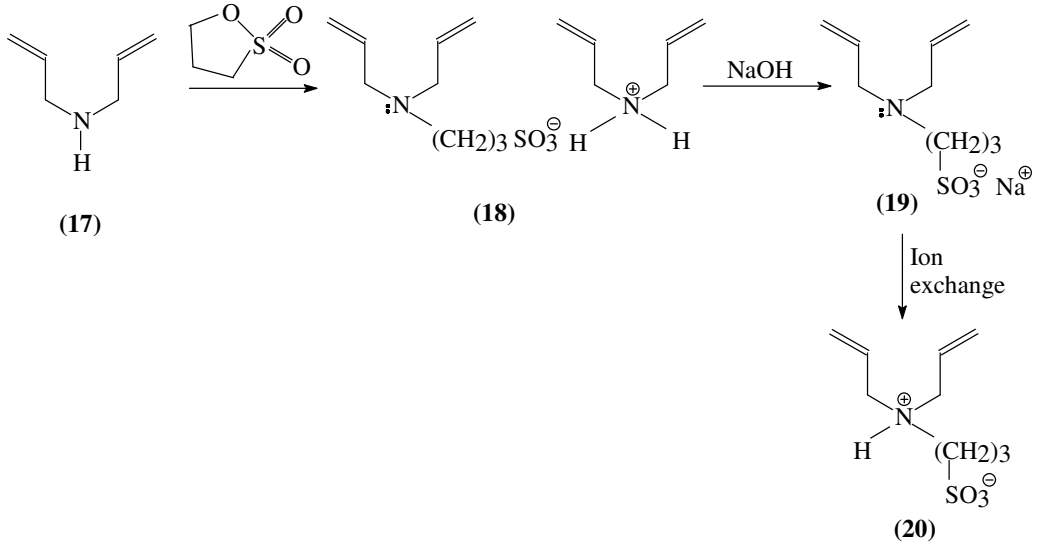
Complexation behavior of proteins with polyampholytes using turbidimetric titration has been investigated [89]. Acrylic polyampholytes have been used for protein separation [90]. Recent [91] study also includes the thermodynamic investigation of the sorption of Fe^{3+} and Cu^{3+} ions by a fibrous polyampholyte.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis of Monomer Precursor (19).

1,3-propanesultone, on treatment with two equivalents of the diallyl amine **17** gave the salt **18,** which on treatment with one equivalent of sodium hydroxide, afforded sodium 3-(*N, N*-diallylamino) propanesulfonate **19** in excellent yield (90%) (Scheme 6).



Scheme 6

The monomer is a crystalline solid and found to be hygroscopic. The monomer is found to be soluble in methanol but insoluble in acetone. The IR spectrum of monomer **19** is shown in Appendix A (I). The IR spectrum indicates the presence of the sulfonate group by its characteristic bands at ~1200 and ~1040 cm^{-1}. ^{1}H NMR, ^{13}C NMR, off resonance and decoupled ^{13}C NMR are shown in Figures 1, 2 and 3 confirms the structure of the monomer **19.** The thermal gravimetric analysis of a monomer sample is shown in Figure 4. The monomer is found to be stable upto 270 °C.

3.2 Synthesis of Zwitterionic Monomer (20).

The precursor molecule **19**, upon cation exchange using cleaned (deionized water and filter) Dowex50 wx8 as a cation exchange resin, gave the zwitterionic monomer, sulfobetaine **20** (95%). (Shown in Scheme 6).

The zwitterionic monomer **20** was found to be soluble in water and methanol but insoluble in acetone. The IR spectrum of monomer **20** is shown in Appendix A (II). The IR spectrum indicates the presence of the sulfonate group by its characteristic bands at ~1200 and ~1040 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra shown in Figures 5 and 6, which confirm the structure of the monomer **20.**

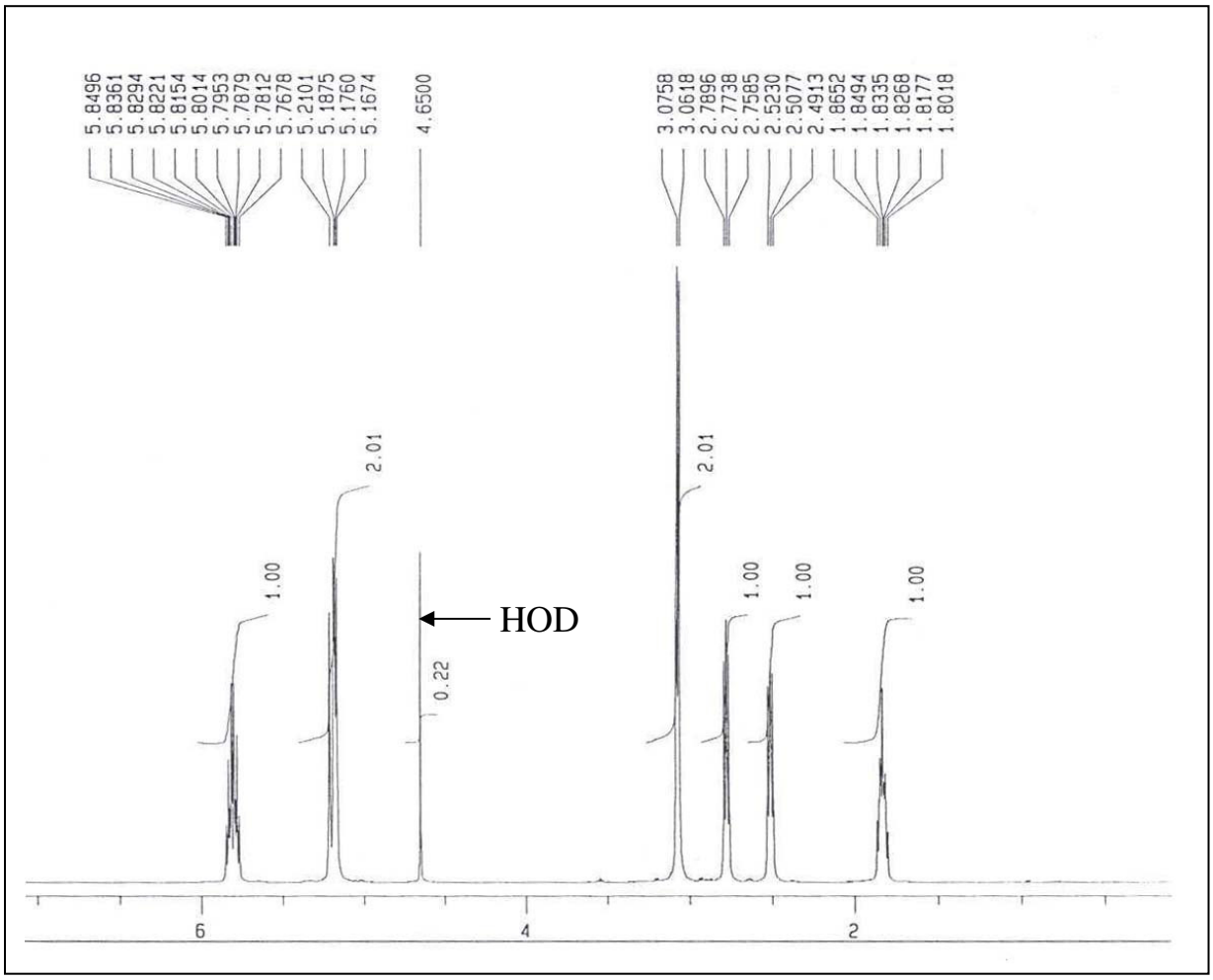


Figure 1: ^{1}H NMR Spectrum of Monomer **19** in D_2O at 20 °C

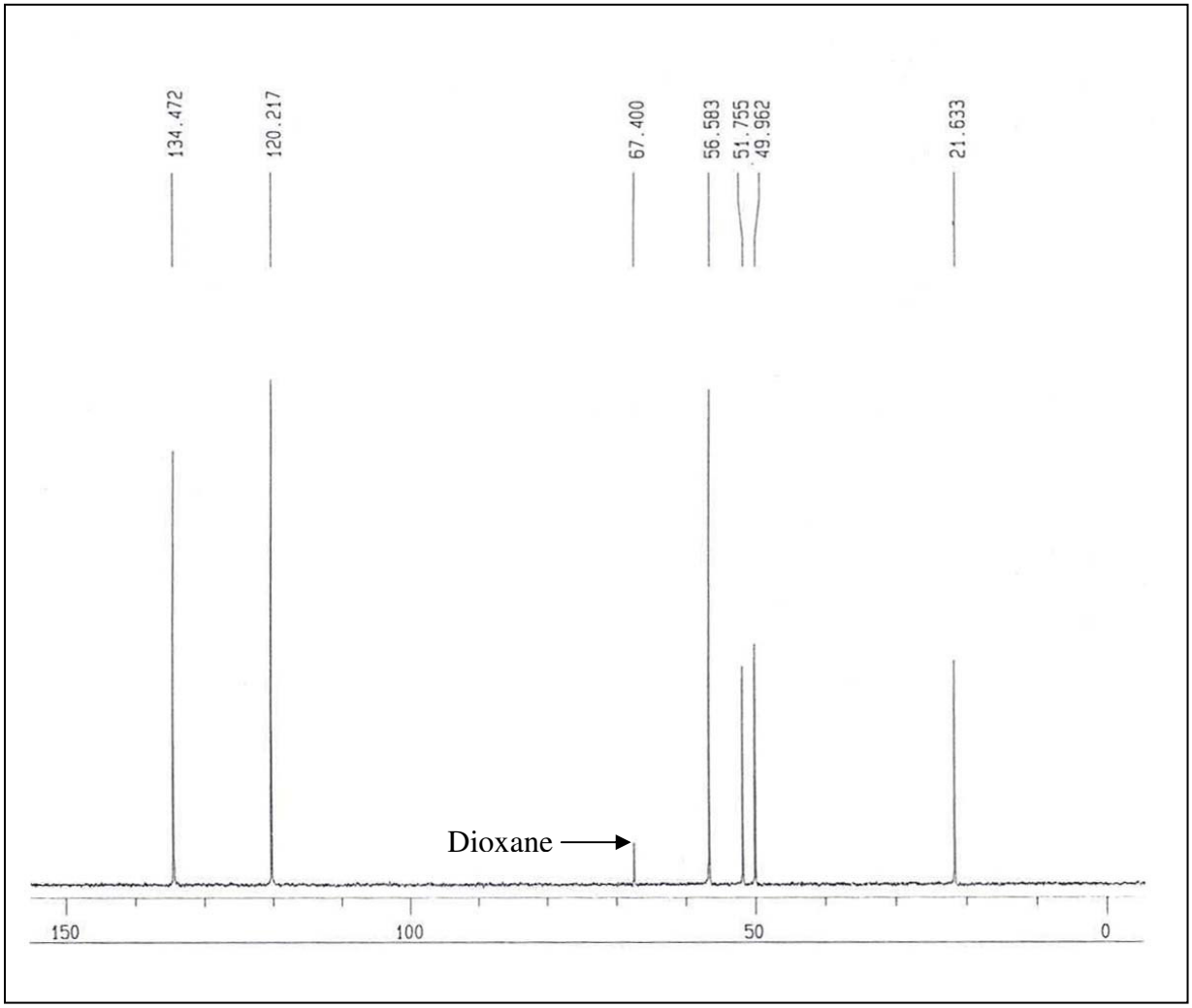


Figure 2: ^{13}C NMR Spectrum of Monomer **19** in D_2O at 20 °C

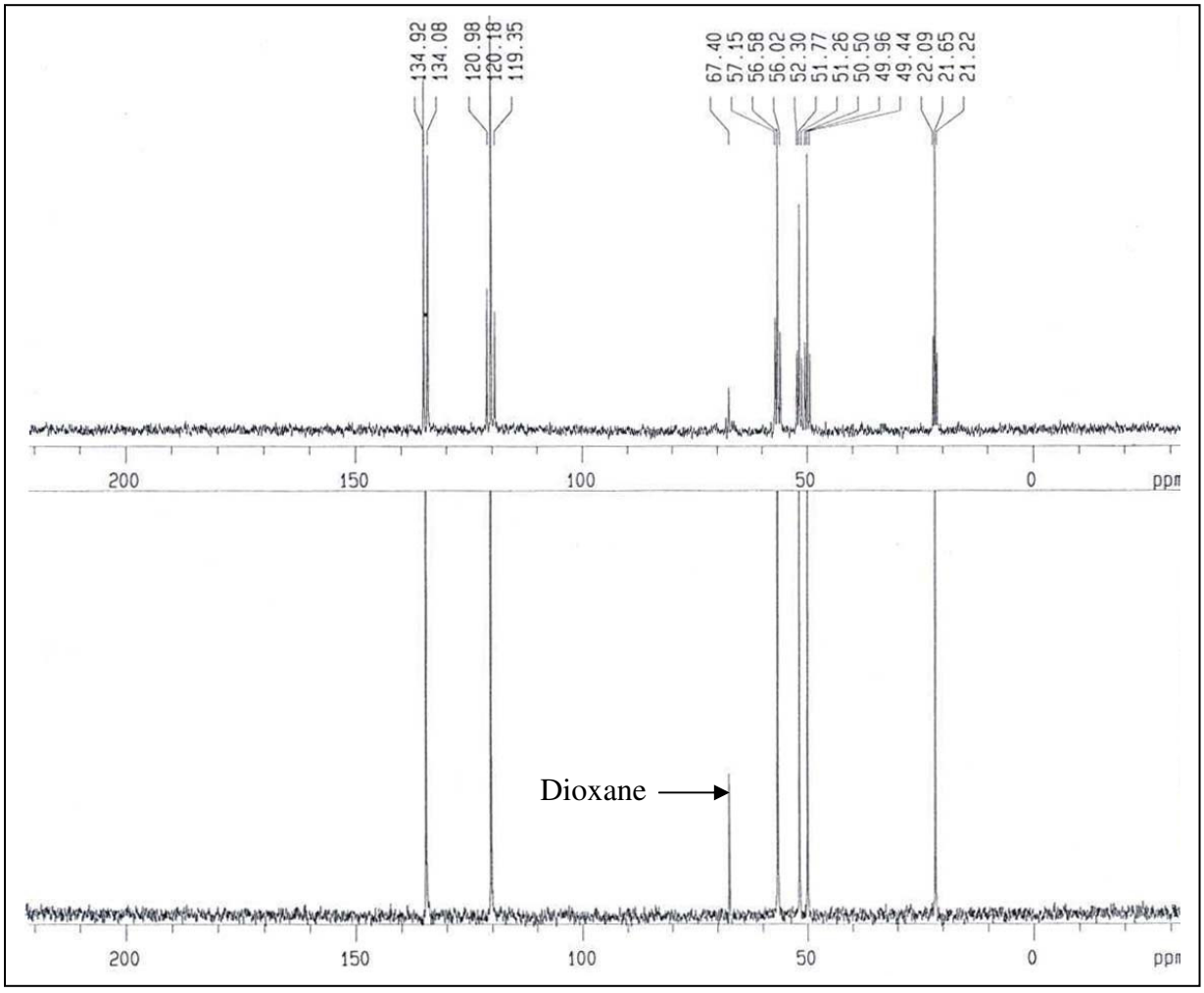


Figure 3: Off resonance and decoupled ^{13}C NMR Spectrum of Monomer **19** in D_2O at 20 °C

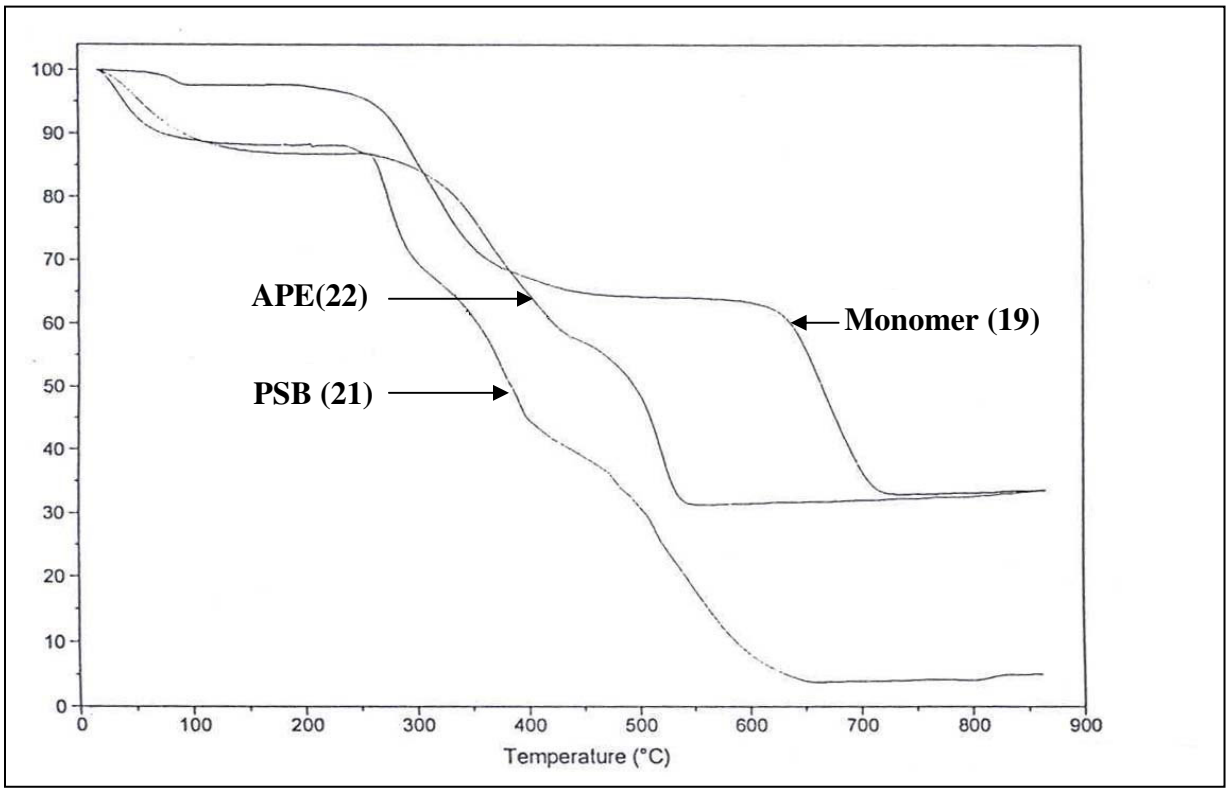


Figure 4: TGA of the Monomer **19**, Polysulfobetaine (PSB) **21** and anionic polyelectrolyte (APE) **22**.

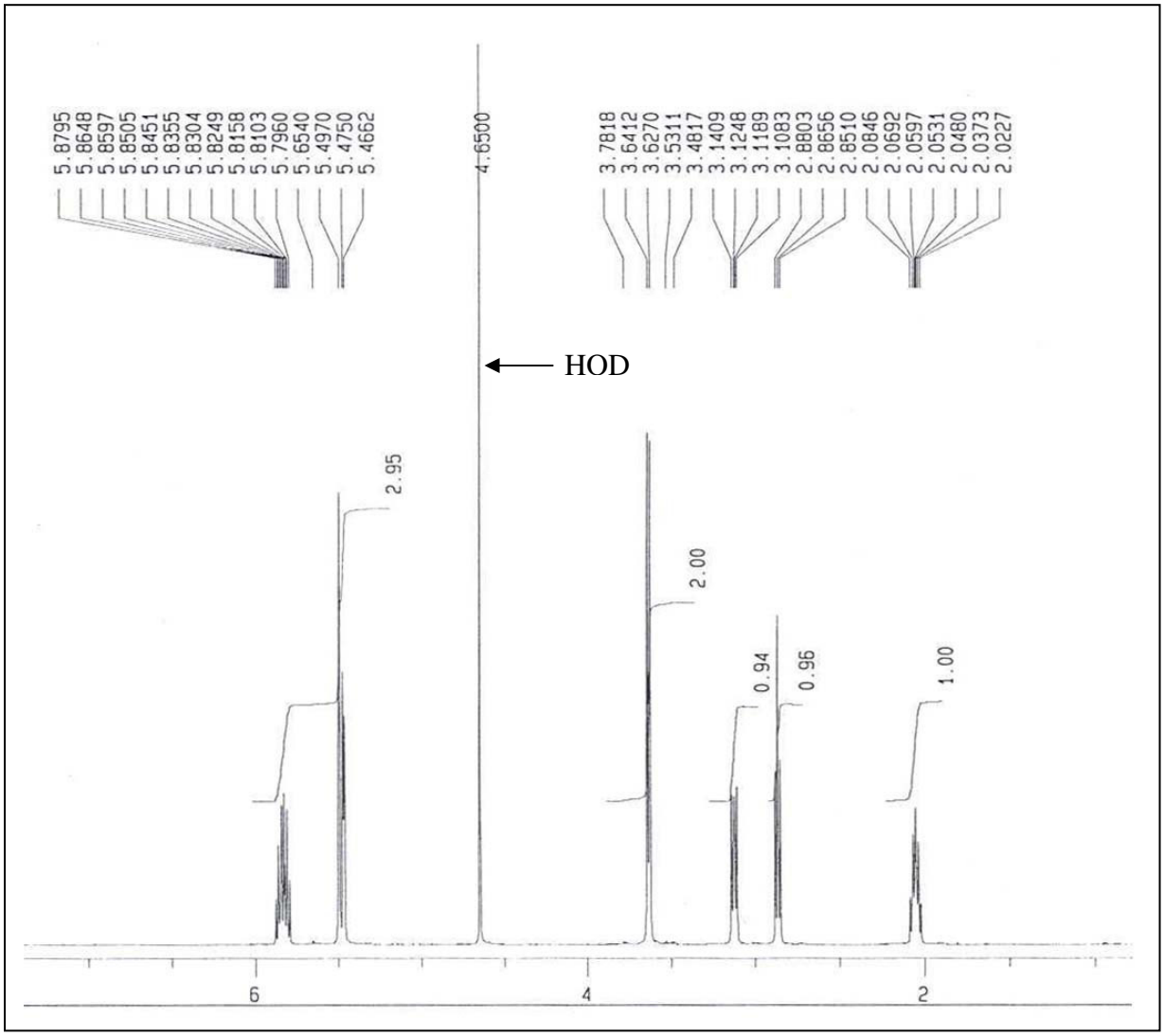


Figure 5: ^{1}H NMR Spectrum of Zwitterionic Monomer **20** in D_2O at 20 °C.

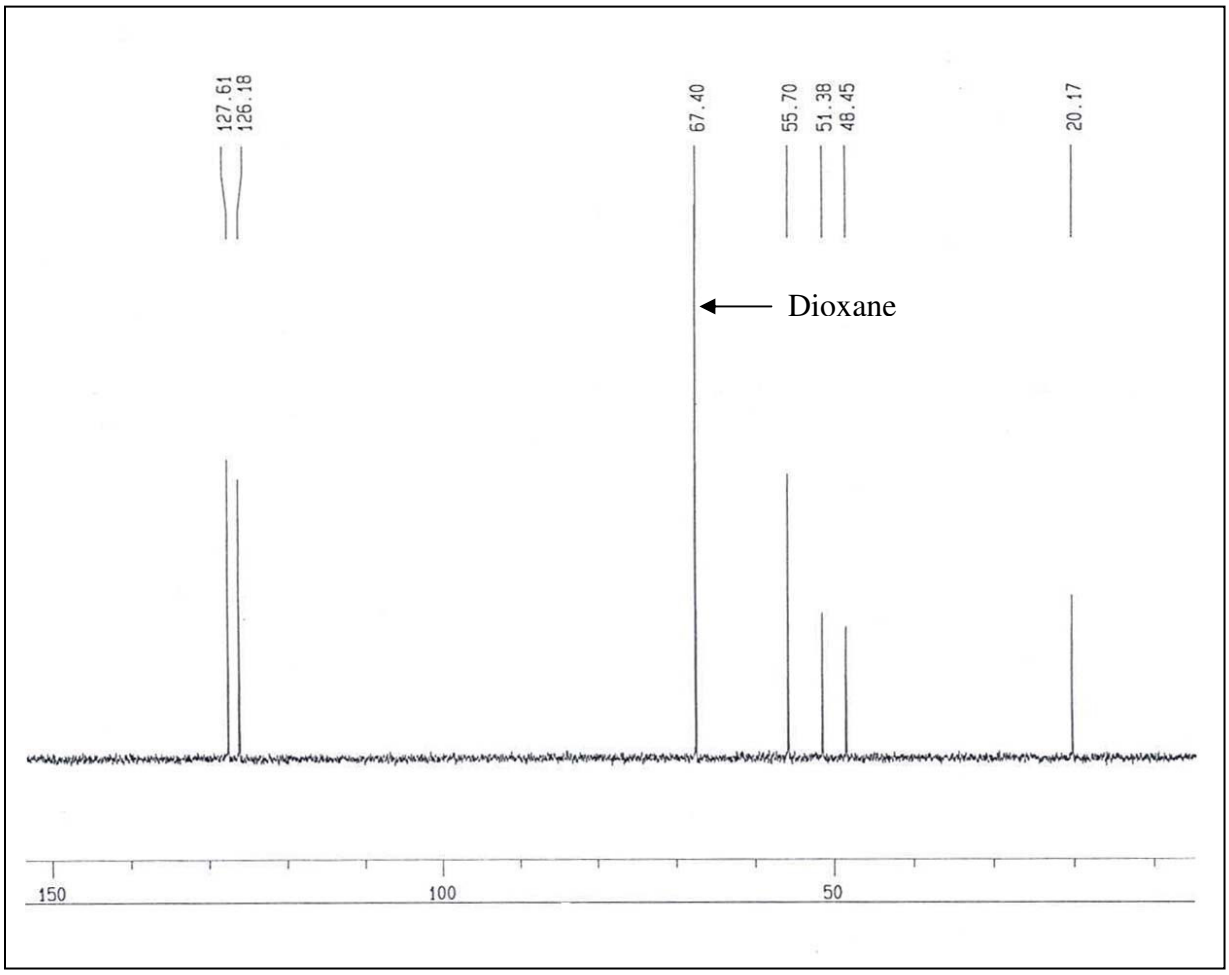
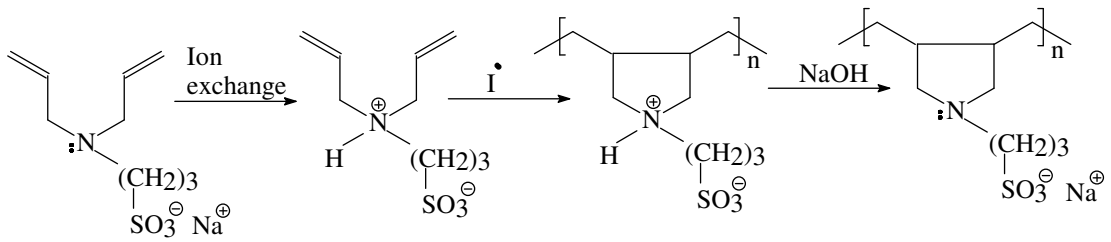


Figure 6: ^{13}C NMR Spectrum of Zwitterionic Monomer **20** in D_2O at 20 °C.

3.3. Synthesis and Characterization of Polysulfobetaine (PSB) 21 and Corresponding anionic Polyelectrolyte (APE) 22.

The monomer was subjected to cyclopolymerization reaction with *t*-butylhydroperoxide as an initiator to give the polysulfobetaine (PSB) **21** in very good yields. The PSB **21**, upon neutralization with sodium hydroxide, was converted into the corresponding anionic polyelectrolyte (APE) **22** (Scheme 7).



(19) **(20)** **(21)** **(22)**

Scheme 7

The results of the polymerizations under various conditions and the intrinsic viscosities of the resultant polymers **22** are given in Table 1. Most of the polymerizations were run in the presence of NaCl that prevents precipitation of the polymers during the reactions. As is evident from the Table 1, the highest yield and viscosity value are obtained for the polymerization reaction under entry 11 with a monomer concentration of 75% (w/w) (cf. entries 1, 3 and 11). The viscosity value increases slightly by keeping the initiator concentration constant and decreasing the molarity of the NaCl (cf. entries 9, 11-13).

TABLE 1: Effect of Concentration of Monomer and Initiator [tertiary butyl hydro peroxide, (TBHP)], Sodium Chloride, and Hydrogen Chloride on Cyclopolymer ization of the Monomer **20.**

Entry	Monomer[a] Concentration (%w/w)	NaCl (M)	HCl (mmol)	TBHP (mg)	Yield,[b,c] (%)	Intrinsic Viscosity[d] (dl g^{-1})
1	60	3	0	10	78 (55)	0.228
2	60	7	0.5	50	44 (35)	0.0750
3	65	3	0	10	80 (61)	0.270
4	65	7	0.5	50	30 (19)	0.0576
5	65	7	0.5	85	52 (40)	0.0590
6	75	0	0.5	85	85 (65)	0.117
7	75	3	0.5	85	72 (57)	0.115
8	75	3	0	85	95 (75)	0.174
9	75	7	0	10	35 (24)	0.117
10	75	3	0	50	93 (74)	0.222
11	75	3	0	10	86 (72)	0.338
12[c]	75	1.5	0	10	86 (69)	0.333
13	75	0.7	0	10	88 (73)	0.378
14	75	0.7	0	5	77 (65)	0.521
15	75	0.35	0	5	87 (71)	0.510
16	75	0.35	0	3.5	83 (76)	0.570
17	75	0	0	85	74 (61)	0.214

[a]Polymerization reactions were carried out using 7.5 mmol of the monomer in aqueous medium at 80 °C for 24 h followed by 90 °C for 24 h.
[b]Determined by ^{1}H NMR analysis. Isolated yields are written in parentheses.
[c]The yield after 24 h at 80 °C was found to be 76% (by ^{1}H NMR), which was changed to 86% after additional heating at 90 °C for 24 h. Further heating did not increase the yield.
[d]Viscosity of 1-0.125 % polymer **(21)** solution in the presence of 1 equivalent of NaOH in 0.1 N NaCl at 30 ^{o}C as measured with an Ubbelohde viscometer (K=0.005718).

In some polymerization reactions, HCl was added in order to ensure the complete protonation of the nitrogen; however, there were no improvement in the yields (cf. entries 7 and 8).

The IR Spectrum of the polysulfobetaine (PSB) **21** is displayed in Appendix A (III). The IR spectrum indicates the presence of the sulfonate group by its characteristic bands at ~1200 and ~1040 cm^{-1}. ^{1}H NMR and ^{1}H NMR decoupled ^{13}C NMR Spectrum of the polysulfobetaine (PSB) shown in Figure 7(a) and 8(a) confirms the structure of the polysulfobetaine **21**. The absence of any residual alkene proton or carbon signal in the spectra suggested the degradative chain transfer process [92] for the termination reaction.

The polysulfobetaine **21** is a hygroscopic solid and has the following onset of thermal decomposition (closed capillary): the color changed to brownish black at 275 °C, but the polymer did not melt or char up to 400 °C. The thermal gravimetric analysis of the polysulfobetaine (PSB) **21** samples, shown in Figure 4 (vide supra), supports the melting point data.

The IR Spectrum of the anionic polyelectrolyte (APE) **22** is displayed in Appendix A(IV). The IR spectrum of the anionic polyelectrolyte (APE) **22** indicates the presence of the sulfonate group by its characteristic bands at ~1200 and ~1040 cm^{-1}.

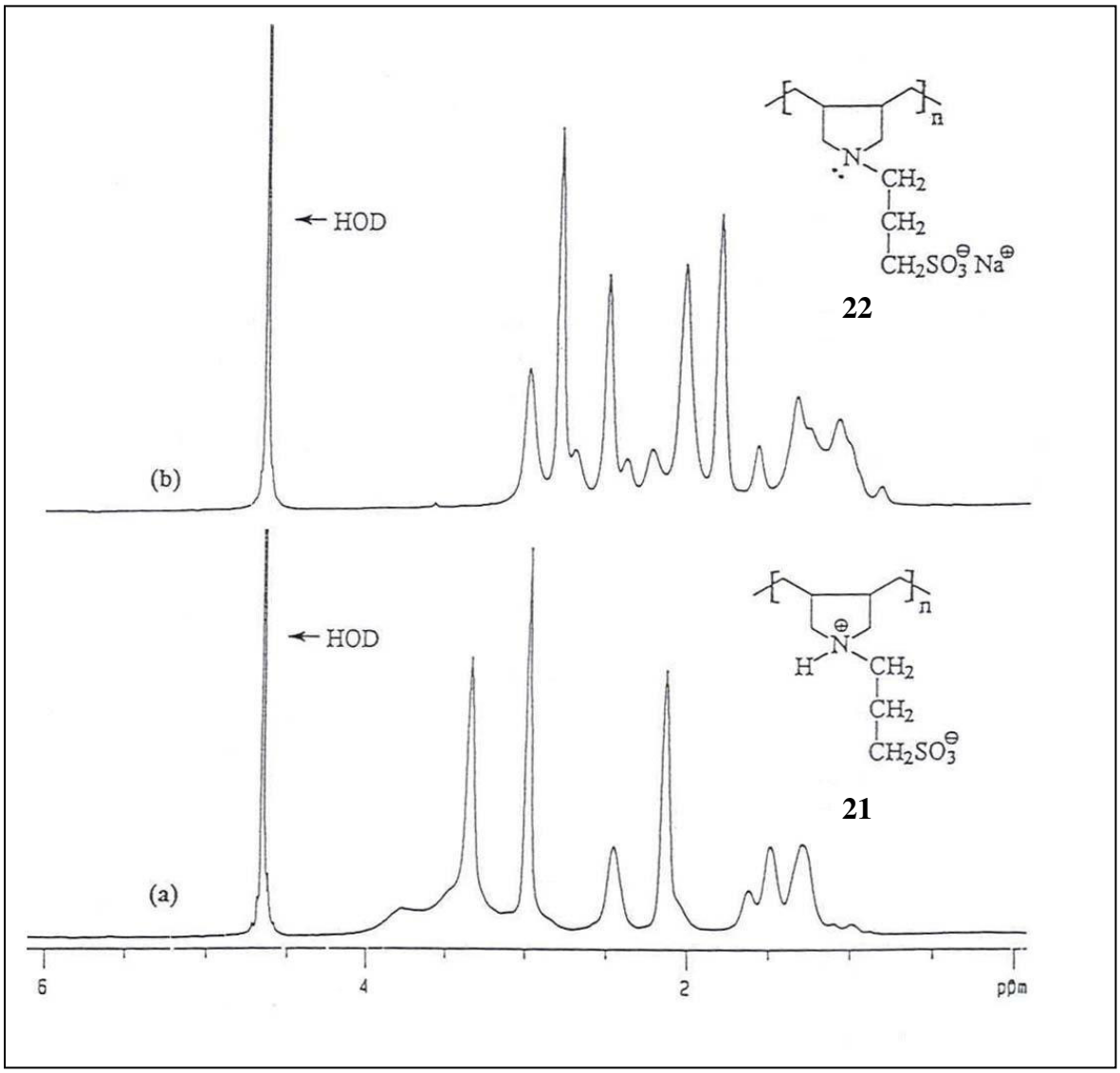


Figure 7: ^{1}H NMR Spectrum of (a) Polysulfobetaine **21** (in the presence of sufficient concentration of NaCl) and (b) Anionic Polyelectrolyte (APE) **22** in D_2O at 20 °C.

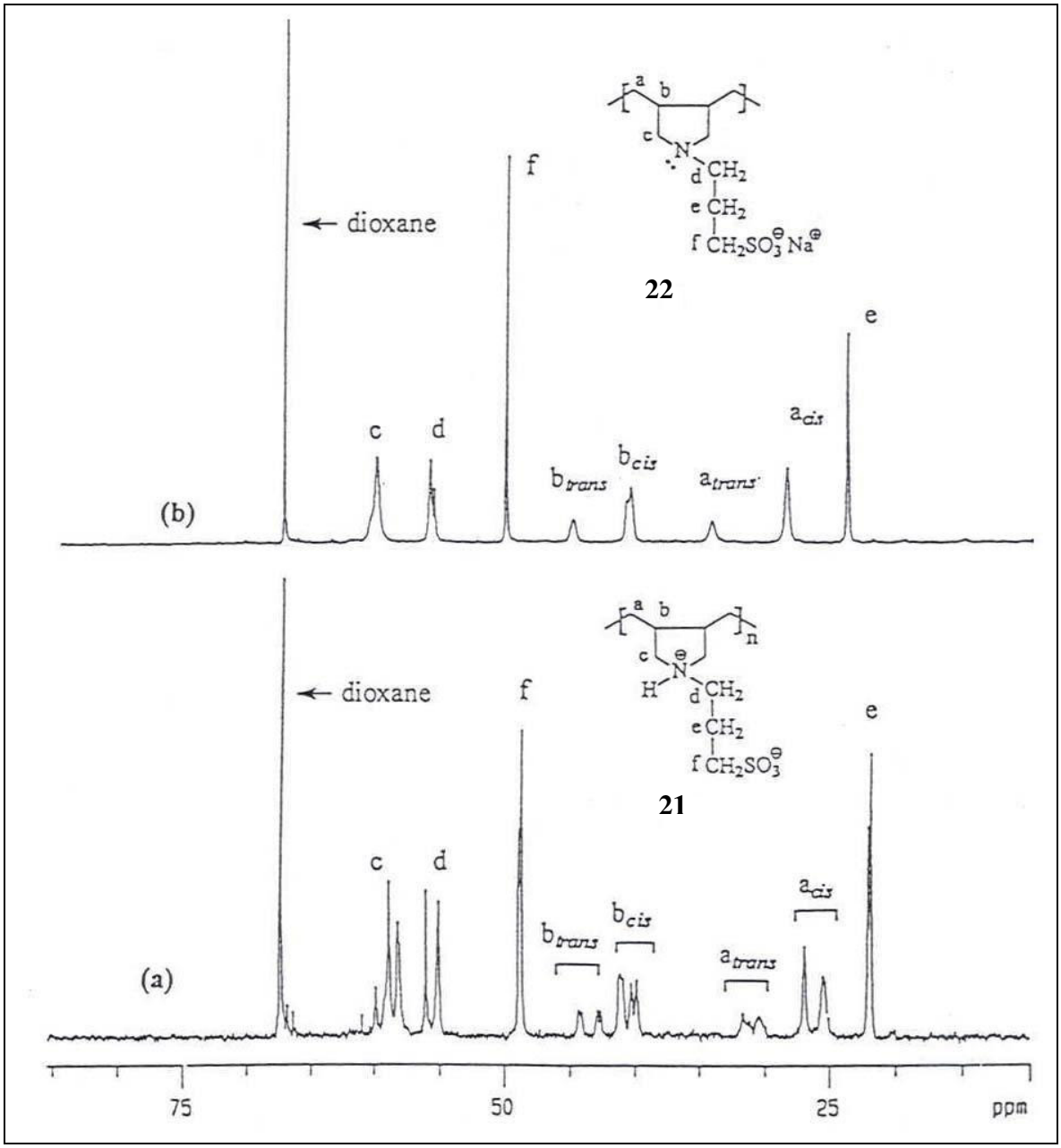


Figure 8: ^{1}H NMR decoupled ^{13}C NMR Spectrum of (a) Polysulfobetaine **21** (in the presence of sufficient concentration of NaCl) and (b) Anionic Polyelectrolyte (APE) **22** in D_2O at 20 °C.

^{1}H NMR and ^{1}H NMR decoupled ^{13}C NMR Spectrum of the anionic polyelectrolyte (APE) **22,** is shown in Figure 7(b) and 8(b), confirm the structure of the anionic polyelectrolyte (APE) **22**. The absence of any residual alkene proton or carbon signal in the spectra suggested the degradative chain transfer process [92] for the termination reaction.

The anionic polyelectrolyte (APE) **22** is a white solid, and has the following onset of thermal decomposition (closed capillary): the color changed to blackish brown at 350 °C, but the polymer did not melt or char up to 400 °C. The thermal gravimetric analysis of the anionic polyelectrolyte (APE) **22** samples, shown in Figure 4 (vide supra), supports the melting point data.

Among all the polymerization reactions, the highest viscosity value was obtained under entry 16; the Table 1 (vide supra) suggests that the intrinsic values increase with decreasing concentrations of both the NaCl and initiator at a constant monomer concentration (cf. 9, 11-16). In the absence of NaCl, however, the polymer yields become low unless a high concentration of the initiator was used (entry 17).

The proton signals of PSB **21** are, as expected, shifted downfield in compare to APE **22** due to the presence of positively charged nitrogen in the former. The assignments of the ^{13}C peaks are based on earlier works [2,6,27,70] on quaternary ammonium salt monomers that undergo cyclopolymerization to afford kinetically favorable five-membered ring structures. The use of the amine salt monomer in this

work, however, does not change the preference the spectral data point to the dominating (if not exclusive) formation of the pyrrolidine rings.

Integration of the relevant peaks in the ^{13}C spectrum yielded a 76/24 cis-trans ratio of the ring substituents, which is similar to that observed for the polymers derived from quaternary ammonium salts [27,28]. The substituents at the C-b of the polymers **21** and **22** can either be in the symmetrical *cis* or unsymmetrical *trans* dispositions (Figure 8). The unequal splitting of the *cis* form can be attributed to the difference in the configuration at N^+; - the *cis* substituents at C-b being *cis* or *trans* to the N-$(CH_2)_3SO_3^-$ in unequal proportion. Only one form is possible for the unsymmetrical minor *trans* isomer, and its C-b and C-b' signals show two weak lines of equal intensity [Figure 8(a)]. However, the polymer **22**, with trivalent nitrogen, undergoes fast nitrogen lone pair inversion in the NMR time scale, and as such the N-$(CH_2)_3SO_3$ group looses its stereochemical integrity, and the splitting of the carbon signals in the *cis* or *trans* forms is not observed [Figure 8(b)].

The solubility behavior of the PSB **21** and APE **22** are shown in Table 2. The APE **22** was found to be very soluble in most of the protic solvents except methanol and acetic acid. Like the overwhelming majority of reported [23,35,36] polybetaines, polysulfobetaine **21** was found to be insoluble in water, as well as in most of the protic solvents except formic acid and formamide. In three separate solubility tests, a sample of the polymer PSB **21** (80 mg) was soaked in 4 cm^3 of deionized water, 0.1 N NaCl and 0.1 N HCl at 25 ºC for 48 h. In each case, the polymer was recovered almost quantitatively,

TABLE 2: Solubility[a,b] of polysulfobetaine **21** and Corresponding Anionic Polyelectrolyte **22**

	ε	PSB **21**	APE **22**
Water	78.4	-	+
Methanol	32.3	-	-
Formic acid	58.5	±	±
Formamide[c]	111.0	+	+
Ethylene glycol	37.3	-	+
Triethylene glycol	23.7	-	+
Acetic acid	6.15	-	-

[a]2% (w/w) of polymer-water mixture (solution) was made after heating the mixture at 70 °C for 1 h and then cooling to 23 °C.

[b]'+' indicates soluble; '-' indicates insoluble; '±' indicates partially soluble.

thus indicating its virtual insolubility in these aqueous systems. However, as anticipated for zwitterionic polymers, PSB **21** was found to be soluble in aqueous solutions of HCl and various salts of sufficient strengths including divalent cation such as Ca^{2+}, which is known to precipitate out polyelectrolytes.

The low molecular weight anions and cations of the added electrolyte enter and partially neutralize a portion of the intra-chain interactions in PSB, thus allowing the collapsed coil in pure water to expand in the presence of small ions. For various salts, the critical minimum salt concentrations (CSC) required to promote water solubility of PSB **21** at 23 °C are shown in Table 3. For a common anion, Cl^-, the sequence of increasing solubility power (decreasing order of CSC values) was found to be:

$$Li^+ < H^+ < NH_4^+ < Ca^{2+} < Na^+ \approx K^+.$$

The Ca^{2+} is placed before Na^+ because each mole of the former is associated with two moles of the chloride ions; the anions are known to play a more dominant role in deciding the solubility behavior. The hydration shell of the cations, especially the H^+, Li^+ and Ca^{2+}, in water is generally fairly large due to their large charge/radius ratio, and presumably cannot approach close enough to effectively neutralize the charge on the sulfonate group [35]. For a common cation, K^+, the CSC values are very sensitive to the nature of the anions. The sequence of increasing solubilizing power was found to be:

$$Cl^- < Br^- << I^-$$

TABLE 3: Critical Salt Concentration for aqueous Solutions of Poly sulfobetaine **21** at 23 °C.

Salt	CSC (M)
LiCl	1.04
NaCl	0.670
KCl	0.638
KBr	0.331
KI	0.135
NH_4Cl	0.718
$CaCl_2$	0.541
HCl	0.940

The concentration of KCl required to promote water solubility was found to be 4.7 times more than that of KI. The iodide anion is the most polarizable (soft). Therefore, it is particularly effective in neutralizing ionic crosslinks, increasing the solubility of the PSB. There is a considerable difference in the concentration of common electrolytes required to promote solubility of PSB **23**; amounts of the salts required were found to be much higher than required in the cases involving polymers of quaternary ammonium sulfobetaines [35,36].

The amine N in PSB **21** is less crowded since H instead of an alkyl group is attached to it, and as such the negatively charged SO_3^- is expected to have closer approach to the positive nitrogen so as to enjoy greater electrostatic attraction. The increased internal neutralization of the charges would make the polymeric backbone tightly coiled and less hydrated. It is interesting to note that the corresponding polycarbobetaine **15** (R^1 = H or Me; m = 1) is readily soluble in salt-free water, 0.1 N NaCl or HCl solution [27,51].

The viscosity data for PSB **21** (entry 16, Table 1) and APE **22** (entry 16, Table 1, obtained by treating the PSB **21** with 1 equiv of NaOH) in deionized water and in NaCl and various other salts of several concentrations were studied. The results are depicted in Figures 9 and 10.

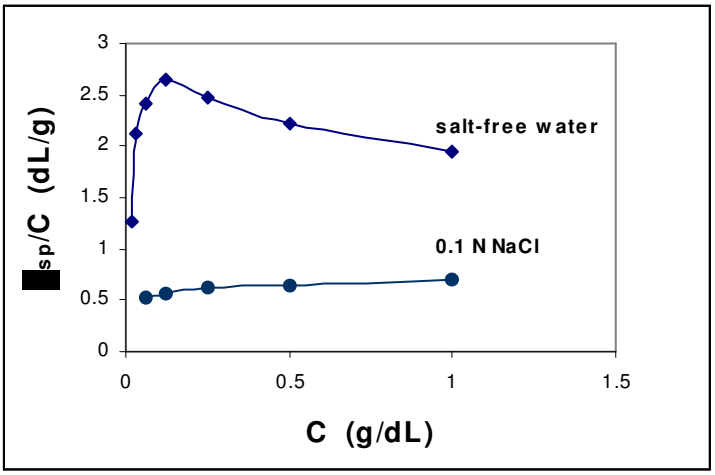


Figure 9: Viscosity behavior of the APE **22** (obtained by the basification of the PSB **21** from entry 16, Table 1) in (a) salt-free water and (b) 0.1 N NaCl at 30 °C with an Ubbelohde Viscometer.

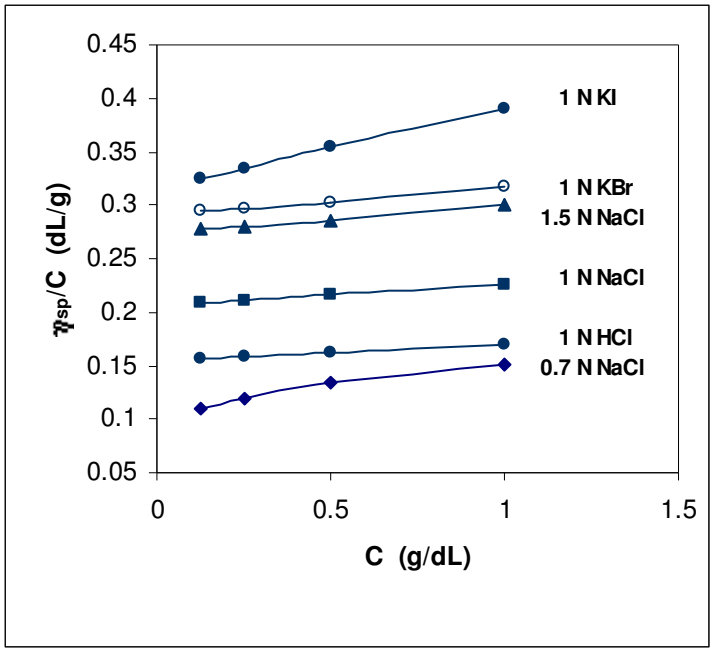
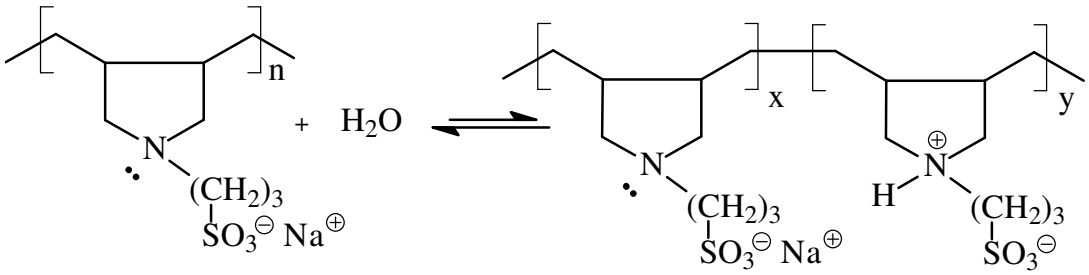


Figure 10: Effect of added salt on the viscosity behavior of the PSB **21** (from entry 16, Table 1) at 30 °C with an Ubbelohde Viscometer.

In the absence of added salt (NaCl), the plot for APE **22** [Figure 9] is typical for a polyelectrolyte; that is, it is concave and upward in the concentrated solution. However, at a higher dilution, the reduced viscosity tends to fall off owing to the formation of the zwitterionic species (as in PSB **21**) by partial protonation of the basic amine nitrogen in APE; the relative proportion of the zwitterions as well as the compactness of the polymer chains are expected to increase with dilution. As expected, the viscosity values for the APE decrease in the presence of added salt NaCl [Figure 9].



22

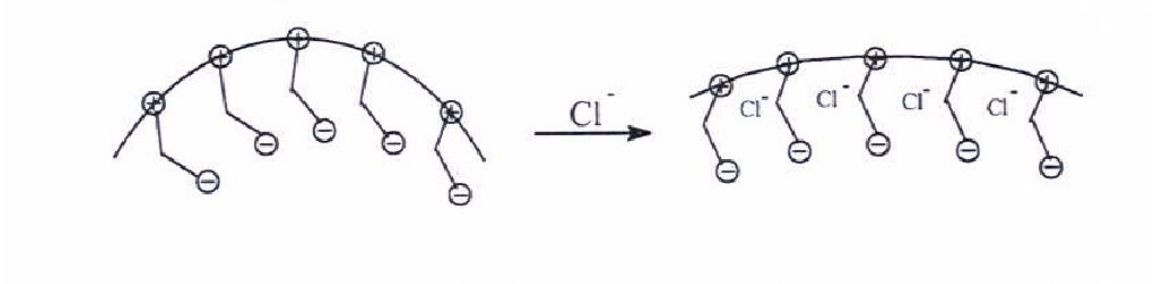
The reduced viscosities of the PSB **21** in aqueous solution containing various added salts (NaCl, KBr, KI) were studied and are illustrated in Figure 10. An increase in the intrinsic viscosity of the PSB **21** with increasing NaCl concentration (0.7, 1.0 and 1.5 N) is a demonstration of the antipolyelectrolyte behavior of the polysulfobetaine **21**. The sequence of increasing intrinsic viscosity is found to be:

$$HCl < NaCl < KBr < KI.$$

Iodide having the smallest charge to radius ratio is more polarizable, hence it can approach closely to the cationic center in the chain thus effectively neutralizing the charge. It is noteworthy that the salt effects on the viscosity and CSC values (discussed previously) are very similar.

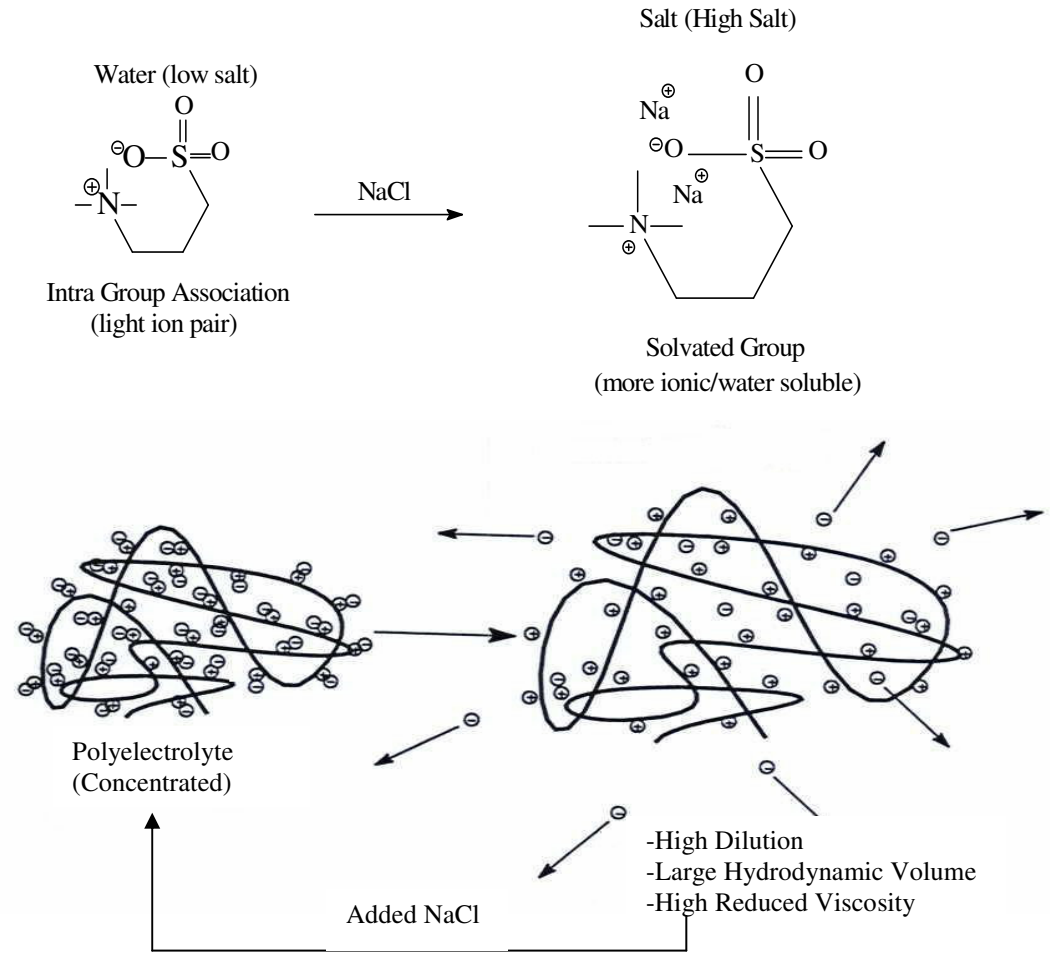
The presence of inorganic salt disrupts the intramolecular interaction of the quaternary ammonium and sulfonate groups, thus causes the tightly coiled polysulfobetaine to behave as a flexible coil as shown in Scheme 8. The addition of salt makes the polysulfobetaine to achieve a more rod-like conformation in order to relieve the repulsion between pendent sulfonate anions.

However, presence of the Na^+ cation can also shield the pendant anions. It seems apparent that while cationic charge on the polymer chain could be effectively neutralized by strongly binding chloride anions, the anionic pendent group is not shielded to that extent by the cation, Na^+. The hydration shell for a positively charged ion (e.g.; Na^+) in water is generally fairly large, hence the distance of closest approach is not sufficient to neutralize effectively the charge on the pendent sulfonate anions so the overall effect of the addition of NaCl is to make the polymer more rod-like hence to increase the intrinsic viscosity of the polysulfobetaine solution. Increase of intrinsic viscosity with increase of added salt indicates increasing chain expansion as a result of columbic interaction between charge of the polymer and the added ions. This type of behaviour has been characterized as " anti-polyelectrolyte".



Scheme 8

The solubility behaviors of PSB **21** were studied in water and dilute salt (NaCl) solution. As expected for all polysulfobetaines, polymer **21** is insoluble in water but dissolves in dilute NaCl solution. This so-called "antipolyelectrolyte effect" is explained in Scheme 9.

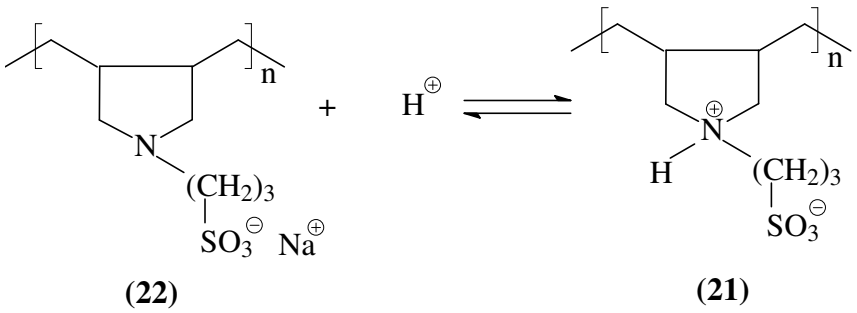


Scheme 9

As shown in Scheme 9, in water the polysulfobetaine molecules assume a collapsed confirmation due to strong intra chain and intra-group associations resulting from electrostatic attractive forces between opposite charges of the zwitterionic moieties.

These associations prevent the polysulfobetaine from dissolving in water. Upon addition of salt, however, these associations are disrupted and the macromolecule assumes as expanded confirmation thereby going into solution.

To gain further information on the conformational transitions, we determined the basicity constants, K^o [Appendix B (I)], and the corresponding n values relative to the protonation of the tertiary amine of both the monomer precursor **19** and APE **22** in salt-free water and 0.1 N NaCl solution.



(22) **(21)**

$$Z^- + H^+ \underset{}{\overset{K}{\rightleftharpoons}} ZH^{\pm}$$

(**22**) (**21**)

$$\log K = pH - \log [(1-\alpha)/\alpha] \quad (1)$$

$$pH = \log K^0 + n \log [(1-\alpha)/\alpha] \quad (2)$$

$$\log K = \log K^0 + (n-1) \log [(1-\alpha)/\alpha] \quad (3)$$

The protonation constant of the amine nitrogen, log K, was calculated at each pH value by the well-known Henderson-Hasselbalch equation (eq 1), where the degree of protonation (α) is the ratio $[ZH^{\pm}]_{eq}/[Z]_o$. The $[Z]_o$ is the initial analytical concentration of the monomeric units in the APE **22** (or PSB **21**), and $[ZH^{\pm}]_{eq}$ is the concentration of the

protonated species at the equilibrium given by $[ZH^{\pm}]_{eq} = C_H^+ - [H^+] + [OH^-]$, where C_H^+ is the concentration of the added HCl; $[H^+]$ and $[OH^-]$ at equilibrium were calculated from the pH value [93]. The typical electrolytes having apparent basicity constants could be described by eq 2, where log K^o is the pH at $\alpha = 0.5$ and $n = 1$ in the case of sharp basicity constants. The linear regression fit of pH versus log $[(1-\alpha)/\alpha)]$ gave log K^o and n as the intercept and slope, respectively.

Simultaneous protonation of the two basic sites was least likely because the basicity constant for the SO_3^- group was less than that of the amine group by at least 8 orders of magnitude. In the case of **19**, the second step protonation constant (log K_2) involving the protonation of SO_3^- was not determined because it would require a large amount of HCl to protonate the very weakly basic sulfonate group to a meaningful extent. In any case, the determination of log K_2 was not possible since the APE **22** started to precipitate in 0.1 N NaCl and salt-free water after the addition of around 0.80 and 0.97 equivalent of HCl, respectively.

The experimental details of the potentiometric titrations are summarized in Table 4. Inserting the value of pH from eq 2 into eq 1 leads to modified Henderson-Hasselbalch equation (eq 3),[94,95] where $n - 1$ gives a measure of the deviation of the studied polymers from the behavior of small molecules showing sharp basicity constants (for molecules having sharp basicity constants, n becomes 1) (Figure. 11).

TABLE 4: Experimental Details for the Protonation of Monomer **19** and Polymers APE **22** (Z^-) at 25 °C in Salt-Free Water and 0.1 N NaCl with 0.1015 N HCl.

Run	$ZH^{\pm}$ [a] or Z^- (mmol)	α Range	pH Range	Points[b]	Log K^{o} [c]	n [c]	R^2, [d]
			Polymers in Salt-Free water				
1	0.4008 ($ZH^{\pm}$)	0.61–0.95	10.66–8.62	10	10.90	1.84	0.9864
2	0.4970 ($ZH^{\pm}$)	0.59–0.97	10.65-8.20	12	10.79	1.76	0.9905
3	0.6293 ($ZH^{\pm}$)	0.56–0.97	10.78–8.24	16	10.83	1.79	0.9825
4	0.4636 (Z^-)	0.57–0.98	10.74–7.35	13	10.78	1.85	0.9853
Average					10.82 (5)	1.81 (4)	
Log K^{e} = 10.82 + 0.81 log [(1-α)/α] For the reaction: $Z^- + H^+ \rightleftharpoons ZH^{\pm}$							
			Monomer in Salt-Free water				
1	0.3028 (Z^-)	0.099–0.89	9.43–7.49	11	8.48	1.03	0.9973
2	0.4129 (Z^-)	0.034–0.79	9.82–7.78	14	8.46	1.02	0.9889
3	0.5224 (Z^-)	0.15–0.92	9.32–7.46	18	8.58	0.97	0.9901
Average					8.51 (6)	1.01 (3)	
Log K^{e} = 8.51 For the reaction: $Z^- + H^+ \rightleftharpoons ZH^{\pm}$							
			Polymers in 0.1 N NaCl				
1	0.3990 ($ZH^{\pm}$)	0.25–0.83	10.69–8.94	14	9.90	1.53	0.9951
2	0.5144 ($ZH^{\pm}$)	0.22–0.84	10.76–8.90	18	9.88	1.55	0.9936
3	0.6197 ($ZH^{\pm}$)	0.17–0.82	10.72–8.91	21	9.78	1.42	0.9982
4	0.5168 (Z^-)	0.23–0.74	10.77–9.27	16	9.95	1.55	0.9992
Average					9.88 (7)	1.51 (6)	
Log K^{e} = 9.88 + 0.51 log [(1-α)/α] For the reaction: $Z^- + H^+ \rightleftharpoons ZH^{\pm}$							
Monomer in 0.1 N NaCl							
1	0.2944 (Z^-)	0.091–0.899	9.16–7.11	11	8.30	1.03	0.9850
2	0.4144 (Z^-)	0.072–0.86	9.33–7.48	14	8.36	0.98	0.9881
3	0.5141 (Z^-)	0.059–0.84	9.42–7.52	17	8.33	1.02	0.9914
Average					8.33 (3)	1.01 (3)	
Log K^{e} = 8.33 For the reaction: $Z^- + H^+ \rightleftharpoons ZH^{\pm}$							

[a]The polysulfobetaine **21** is treated with (one) 1 equivalent of a 0.1046 N NaOH and the resultant APE **22** is then titrated with 0.1015 N HCl.

[b]Number of data points from the titration curve.

[c]Values in the parentheses are standard deviations in the last digit.

[d]R = Corrélation coefficient.

[e]$\log K = \log K^{o} + (n - 1) \log [(1 - \alpha)/\alpha]$.

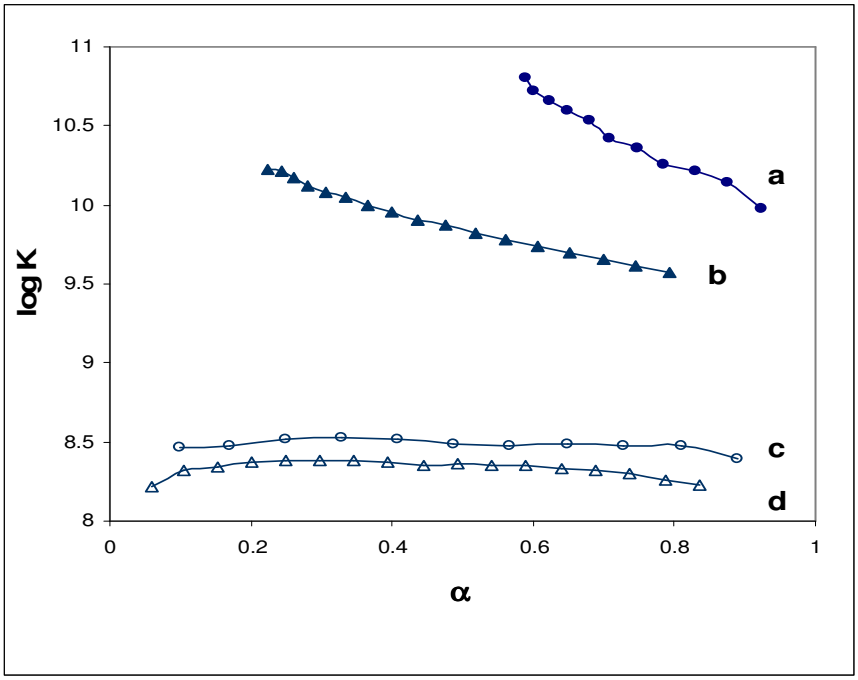


Figure 11: Plot of the apparent log *K* versus α for APE **22** (a) in salt-free water and (b) in 0.1 N NaCl, and that of precursor molecule **19** (c) in salt-free water and (d) in 0.1 N NaCl.

The solution of the anionic polyelectrolyte (APE) **22** was titrated at 25 ^{0}C with 0.1015 M HCl under N_2, and the pH of the solution at each addition was recorded with a Corning 220 pH meter. Basicity constants and the corresponding *n* values as well as the experimental details of the potentiometric titrations are summarized in Table 4. Inserting the value of pH from eq 2 into eq 1 leads to modified Henderson-Hasselbalch equation (eq 3) [94,95] where $n - 1$ gives a measure of the deviation of the studied polymers from the behavior of small molecules showing sharp basicity constants (for molecules having sharp basicity constants, *n* becomes 1) (Figure 11).

Some of the representable graphs (Table 4) for values of *n* and R^2 are shown in Figures 12, 13, 14 and 15. Detailed representation of the data (Table 4) is depicted in appendix B (I-VI).

The basicity constants of this polymer are apparent [94-98] because the *n* values were greater than 1, and as such they decreased with the degree of protonation (α) in salt free water as well as 0.1N NaCl (Fig. 11 a, b)[Appendix B]. The magnitude of *n* reflects the polyelectrolyte effect, and can be regarded as an index of accessibility of the proton to the amine nitrogen during the protonation reaction. The basicity constants for the corresponding monomer **19**, as expected, were found to be "real" with an *n* value of 1, and as such that they are constant with the degree of protonation in salt free water and in 0.1N NaCl (Figure 11 c, d).

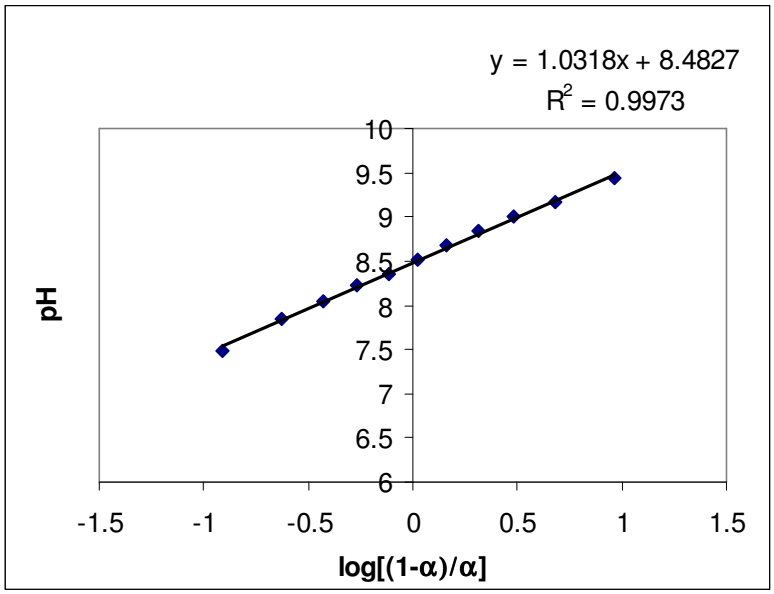


Figure 12: Protonation behaviour of Monomer **19** (Z_0) at 25 °C in salt free water and with 0.1015 HCl. [Appendix B (III)]

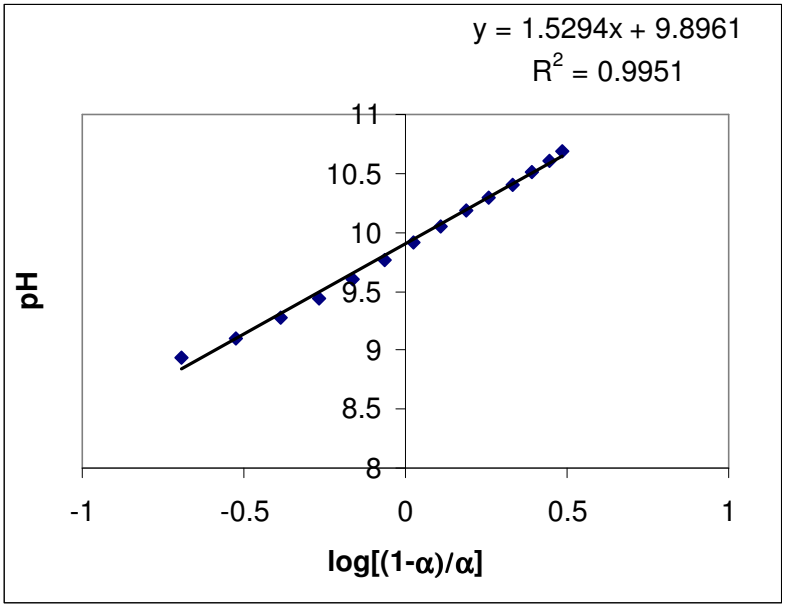


Figure 13: Protonation behaviour of the Polymer **22** (Z^-) at 25 °C in 0.1 NaCl and with 0.1015 HCl. [Appendix B (IV)]

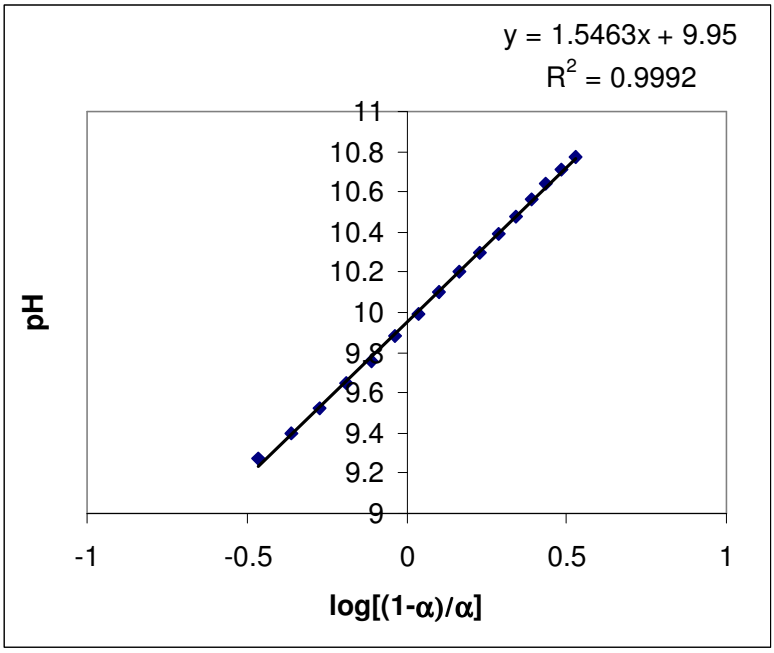


Figure 14: Protonation behaviour of the Anionic Polymer (APE) **22** (Z^-) at 25 °C in 0.1N NaCl and with 0.1015 HCl. [Appendix B (V)]

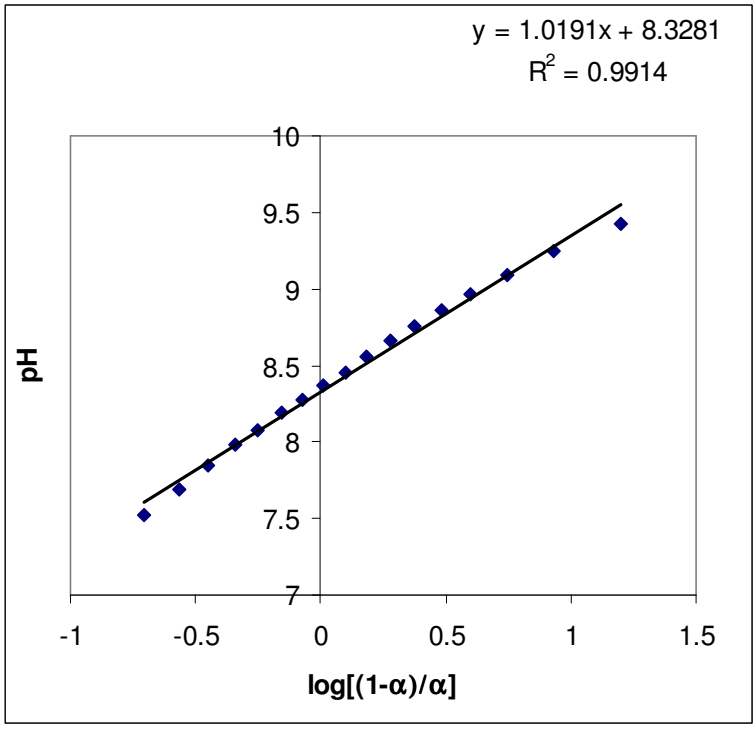


Figure 15: Protonation behaviour of Monomer **19** (Z_0) at 25 °C in 0.1N NaCl and with 0.1015 HCl. [Appendix B (VI)]

The basicity constant (log K^o) of the amine group in APE **22** is higher by almost a unit in salt-free water in compare to 0.1 N NaCl (Fig. 11 and Table 4). The *n* values in salt-free water and 0.1 N NaCl were 1.81 and 1.51, respectively (Table 4).

The *n* values greater than 1 indicated that the approach of the incoming protons to the amine nitrogen groups became more and more difficult as α for the whole macromolecule increased. The basicity constant (log *K*), therefore, decreased progressively because of a decrease in the electrostatic field force as a result of a decreasing overall negative charge density in the macromolecule (Figure 11 a, b).

Several studies [96] have indicated that the entropy effects involving release of water molecules from the hydration shell of the repeating unit that is being protonated dictate the protonation of polymers. The APE **22** in salt-free water is highly extended as indicated by higher viscosity values (Figure 9), and as such more hydrated (more water molecules in each hydration shell) than in salt solution (0.1 N NaCl) where the polymer chain adapts a compact conformation because of screening of the negative charges by the sodium ions. Thus with progressive protonation, the number of water molecules released from the hydration shell of the repeating unit being protonated becomes greater in salt-free water than in 0.1 N NaCl. This is reflected by the higher *n* value (1.81), greater basicity constant (log *K*: 10.82), and greater changes in the basicity constant in salt-free water [Fig. 11(a)] than in the 0.1 N NaCl where the basicity constant and the *n* values are found to be 9.88 and 1.51, respectively. It is to be noted that the log *K* values for the

corresponding monomer precursor **19** were found to be much less; 8.51 (in salt-free water) and 8.33 (0.1 N NaCl).

A viscometric titration of a 0.0228 M (0.5 g/dL) solution of the PSB **21** in the presence of 1 equiv of NaOH at 25 °C is depicted in Figure 16 .The Figure also includes the distribution curves of the different ionized species $ZH^{\pm}$ (PSB **21**) and Z^{-} (APE **22**) calculated from the basicity constants (vide supra) and pH values. Reduced viscosity decreases continuously as the concentration of the zwitterionic species, $ZH^{\pm}$ increases and that of the anionic species, Z^{-}, decreases. The observations presented above are supported by the viscometric studies.

The study of phase diagram was an important step in this work. The phase diagram and the tie lines (A-E) for a system composed of PEG-35,000 and PSB **21** (+0.60 equiv NaOH) in 0.1 N KCl is constructed by turbidity method and ^{1}H NMR technique, [18, 49] respectively. The binodal curve (Figure 17) distinguishes between single- and two-phase regions and provides information about the concentration of both polymers required for protein separation work.

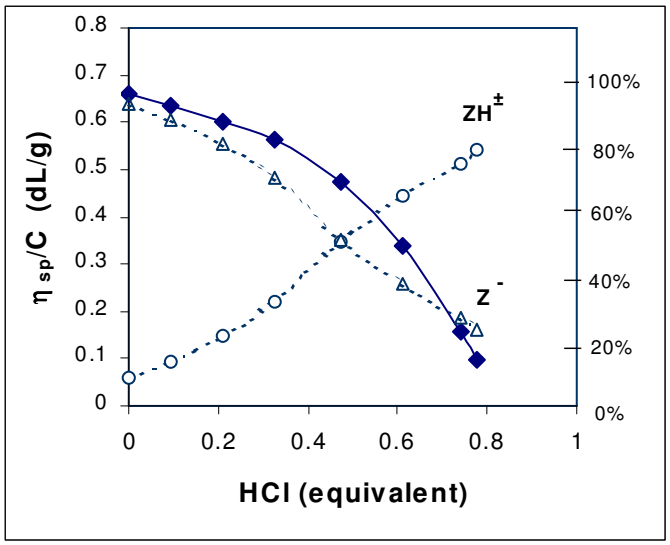


Figure 16: Reduced viscosity (η_{sp}/C) of a 0.0228 M (i.e. 0.50 g/dL) solution of polymer PSB **21** (+1 equiv NaOH) in 0.1 N NaCl (♦) versus equivalent of added HCl at 25 °C. Distribution curves (dashed lines) of the various ionized species calculated from the basicity constants log *K* in 0.1 N NaCl at 25 °C.

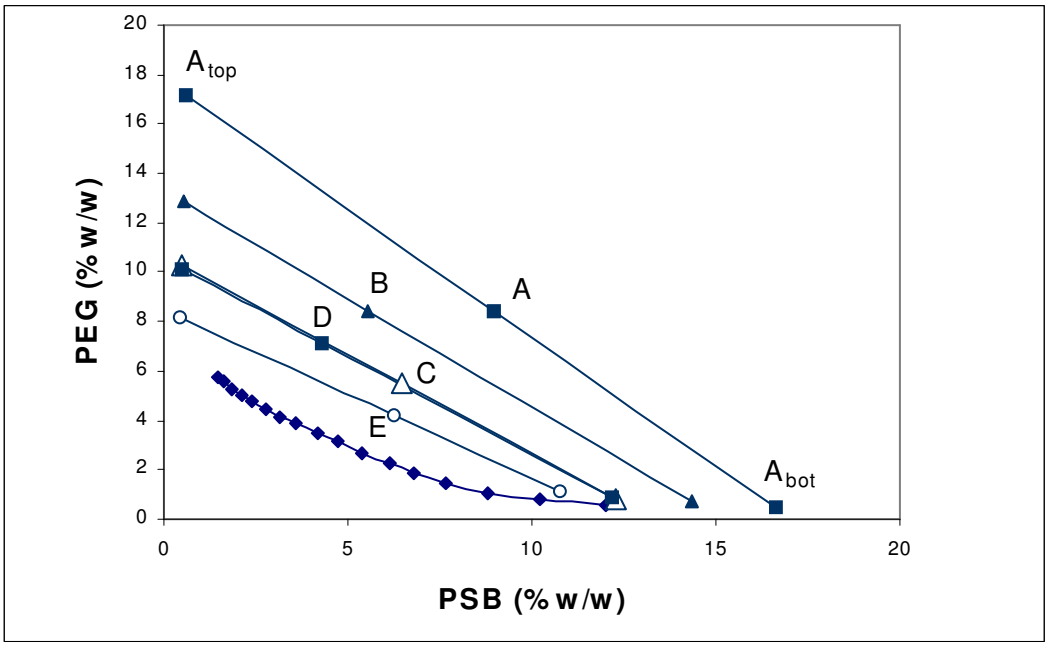
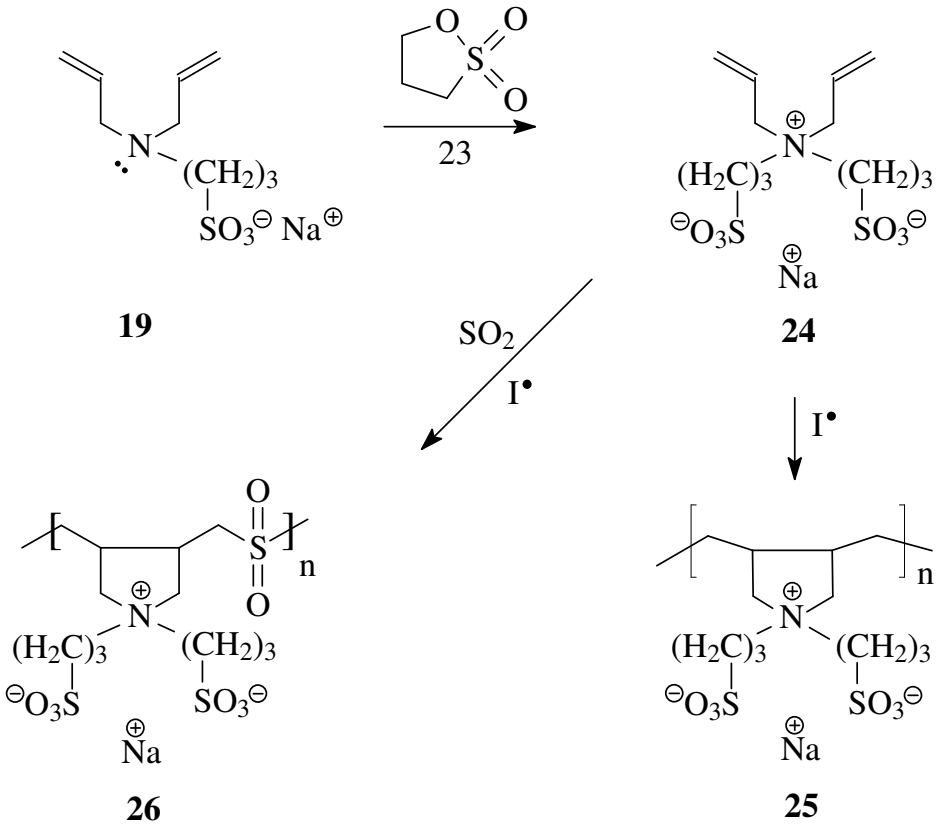


Figure 17: Phase diagram of the system containing PSB **21** (treated with 0.60 equiv NaOH) and PEG-35,000 in 0.1 N KCl at 23 °C.

The phase separation took place at relatively low total polymer concentrations, typically below 10%; phase separation in a low concentration could be useful from an industrial point of view. The PEG and PSB displayed preference to remain in the top and bottom phase, respectively. The tie lines were helpful in constructing two-phases with suitable volume ratio of the top and bottom phases. For instance, the total system represented by the point *A* will have the volume or mass ratio of the top and bottom phases determined by the ratio of length A-A_{bot} and A-A_{top}, respectively. Aqueous two-phase polymer systems as constructed above may offer a friendly environment for the separation [52,53-55] of labile proteins. Purified dextran, used in the most common dextran-poly(ethylene glycol) system for protein separation, is quite expensive and biodegradable [99]. The pH dependent solubility behavior of the new polymer described in this work may allow its effective removal and recycling.

3.4 Synthesis of the Zwitterionic-Electrolytic Monomer (24)

Sodium 3-(*N,N*-diallylamino)propanesulfonate **19,** on treatment with 1,3-propanesultone, afforded the special zwitterionic-electrolytic monomer **24** in excellent yield (90%) (Scheme 10).



Scheme 10

This monomer was found to be soluble in water, methanol, DMF, DMSO but insoluble in acetone, acetonitrile and many other less polar common solvents. Interestingly, the monomer was found to remain in solution in a 90:10 acetonitrile/methanol mixture at 20°C but precipitates out as the solution is heated (~40°C). The IR Spectrum of the zwitterionic-electrolytic monomer **24** is displayed in Appendix A (V). The ^{1}H NMR and ^{13}C NMR spectra are shown in Figures 18 and 19, respectively.

3.5 Synthesis of the PEZ (25)

The monomer **24** was subjected to cyclopolymerization reaction in aqueous solution using *t*-butylhydroperoxide as an initiator to give the poly(electrolyte-zwitterion) (PEZ) **25** in very good yields. The results of the polymerizations carried out under various monomer concentration and the intrinsic viscosities of the resultant polymers **25** are given in Table 5. As is evident from Table 5, the highest yield and viscosity value are obtained for the polymerization reaction under entry 2 with a monomer concentration of 70% (w/w) [Scheme 10].

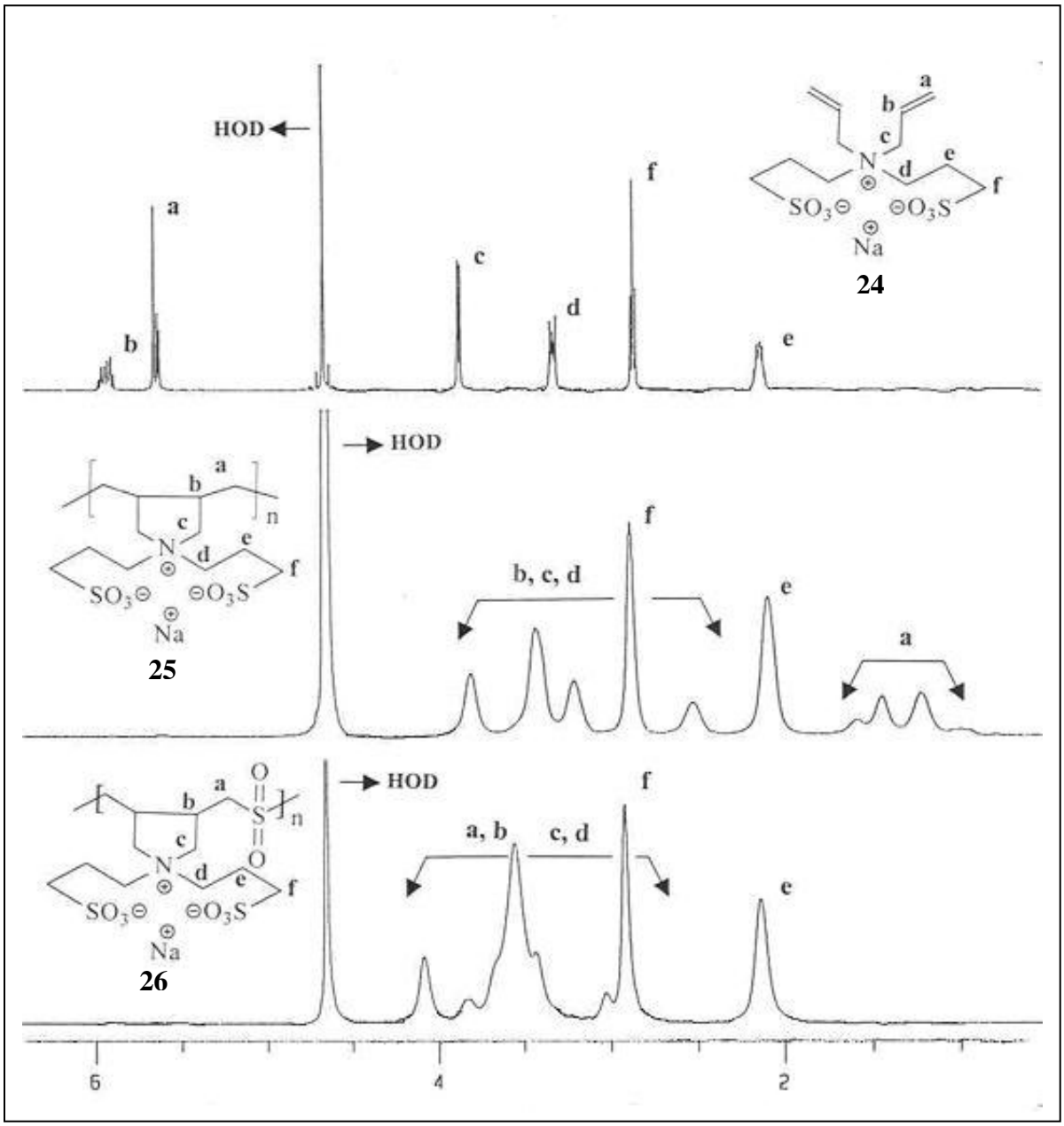


Figure 18: ^{1}H NMR spectrum of the monomer **24**, PEZ **25** and **26** in D_2O.at 20^{o} C.

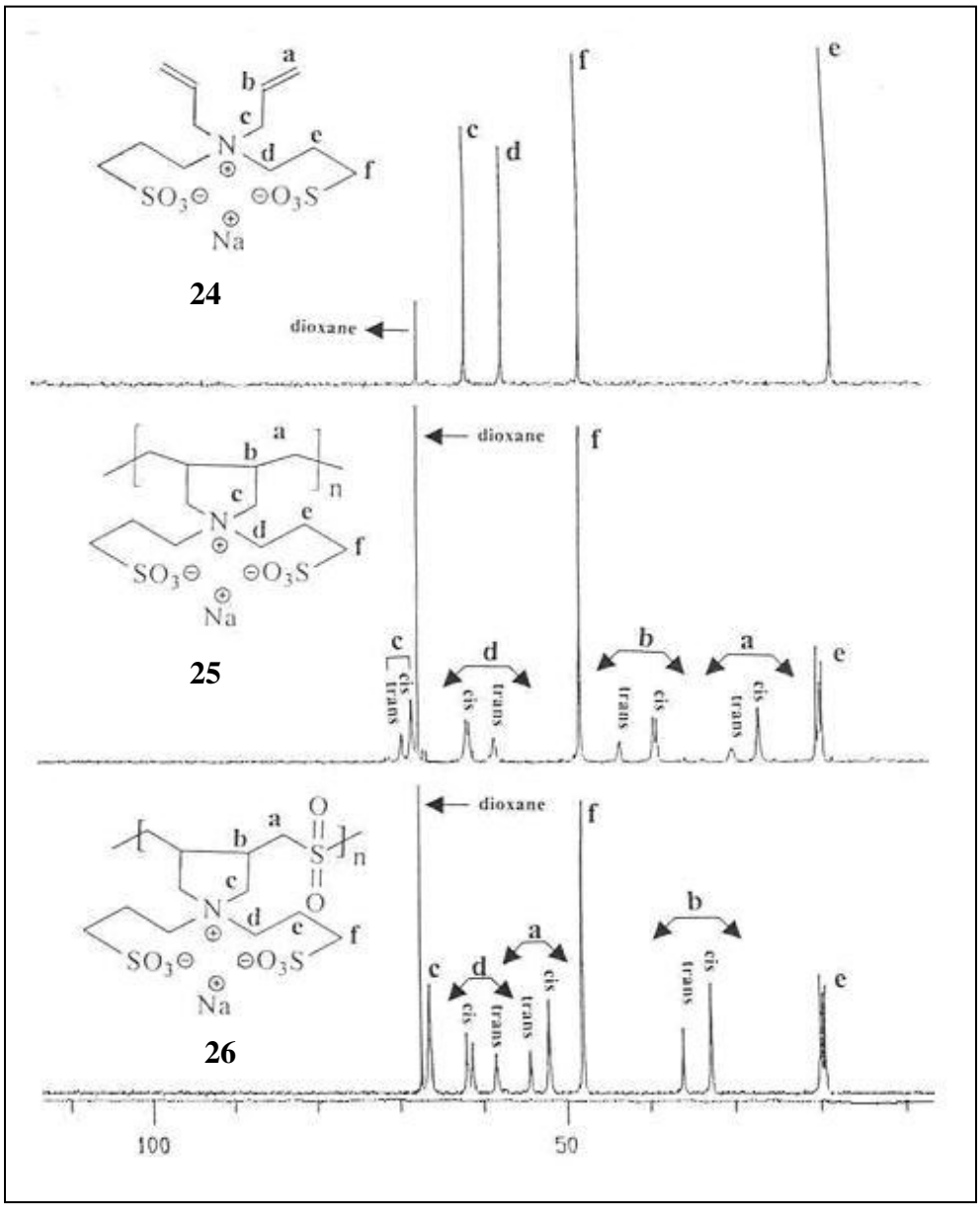


Figure 19: ^{1}H decoupled ^{13}C NMR spectrum of the monomer **24**, PEZ **25** and **26** in D2O at 20°C.

TABLE 5: Effect of Monomer **24** concentration on the cylopolymerization.

Entry	Monomer[a] Concentration (%w/w)	TBHP[b] (mg)	Yield, [c] (%)	Intrinsic Viscosity[d] (dl g^{-1})
1	65	10	78 (63)	0.145
2	70	10	89 (74)	0.161
3	75	10	85 (72)	0.151

[a]Polymerization reactions were carried out using 11 mmol of the monomer in aqueous medium at 70 °C for 20 h followed by 80 °C for 20 h.

[b]Initiator [tertiary butylhydroperoxide, (TBHP)]

[c]Determined by ^{1}H NMR analysis. Isolated yields are written in parentheses.

[d]Viscosity of 1-0.125 % polymer **(25)** solution in 0.1 N NaCl at 30 ^{o}C as measured with an Ubbelohde viscometer (K=0.005718).

3.6 Synthesis of the PEZ Copolymer (26) with SO_2

Cyclopolymerization of the monomer **24**-SO_2 in DMSO using AIBN as the initiator went smoothly to give the copolymer PEZ **26** in excellent yields (Scheme 10). The results of the polymerization under different concentration of the monomer in DMSO and initiator, and the intrinsic viscosities of the resultant polymers are given in Table 6. Lower monomer and high initiator concentration lead to polymers with lower viscosity values.

The IR Spectrum of the poly(electrolyte zwitterions) (PEZ) **25** is displayed in Appendix A(VI). The IR spectra of the PEZ**, 25** and **26**, indicate the presence of the sulfonate group by its strong characteristic bands at ~1190 and ~1047 cm^{-1}. The two strong bands at 1308 and 1132 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit in the copolymer **26,** which is shown in Appendix A (VII). ^{1}H and ^{13}C NMR spectra of the monomer **24**, PEZ **25** and copolymer PEZ **26** are displayed in Figures 18 and 19, respectively.

The absence of any residual alkene proton or carbon signal in the spectra suggested the degradative chain transfer process [92] for the termination reaction. The proton signals of PEZ **26** are, as expected, shifted downfield in compare to APE **24** due to the presence of electron withdrawing SO_2 group in the polymer backbone.

TABLE 6: Effect of concentration of monomer and initiator on the monomer **24**/SO_2 copolymerizartion[a]

Entry Number	DMSO (g)	Initiator[b] (mg)	Yield (%)	Intrinsic Viscosity[c] (dl g^{-1})
1	5.2	35	77 (65)	0.556
2	5.2	55	85 (76)	0.285
3	8.5	55	86 (73)	0.293

[a]Polymerization reactions were carried out in DMSO using 11 mmol each of the monomer and SO_2 at 57 ^{o}C for 24 h.

[b]Azobisisobutyronitrile.

[c]Viscosity of 1-0.0625% polymer solution in the presence of 1 equivalent of NaOH in 0.1 N NaCl at 30^{o}C was measured with a Ubbelohde Viscometer (K = 0.005718).

The assignments of the ^{13}C peaks are based on previous works [2,6,27,70]; the spectral data (specially the number of signals) point to the formation of the pyrrolidine rings rather than the unsymmetrical six-member ring structure. Integration of the relevant peaks in the ^{13}C spectrum yields the *cis/trans* ratio of the ring substituents to be 70/30, which is similar to that observed for the polymers derived from quaternary ammonium salts [27,28].

The solubility behavior of the PEZ **25** and copolymer PEZ **26** are shown in Table 7. Both the homo- and co-polymers were found to be very soluble in majority of the protic solvents except methanol, triethylene glycol and acetic acid. The solubility in water is a demonstration of the electrolytic behavior the PEZs, since the zwitterionic trait [23,35,36] in the polymers are expected to impart insolubility in water.

Viscosity data for PEZ **25** (entry 2, Table 5) is presented in Figures 20 and 21. In the absence of added salt (NaCl), the plot for PEZ **25** is typical for polyelectrolyte i.e. concave upward. In the presence of added salt the viscosity curves become linear as expected of any polyelectrolyte; the intrinsic viscosity values decreases with increase in the NaCl concentration and converge to a minimum at 0.3 N NaCl. The viscosity remains almost the same thereafter in 0.5 and 1 N NaCl solution.

TABLE 7: Solubility[a,b] of PEZ **25** and **26**

Solvent	ε	HOMO **25**	CO **26**
Water	78.4	+	+
Methanol	32.3	-	-
Formic acid	58.5	+	+
Formamide	111.0	+	+
Ethylene glycol	37.3	+	+
Triethylene glycol	23.7	-	-
Acetic acid	6.15	-	-

[a]2% (w/w) of polymer-water mixture (solution) was made after heating the mixture at 70 °C for 1 h and then cooling to 23 °C.

[b]'+' indicates soluble; '-' indicates insoluble.

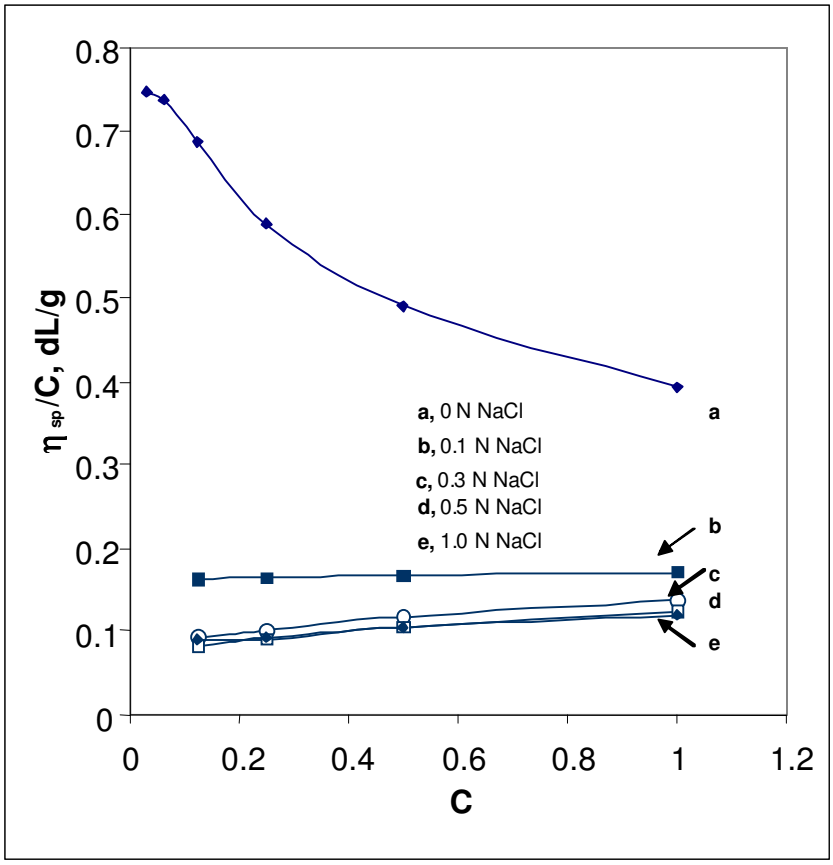


Figure 20: The viscosity behavior of PEZ **25** (entry 2, Table 5) in salt-free water and various NaCl solutions at 30 ^{o}C using an Ubbelohde Viscometer.

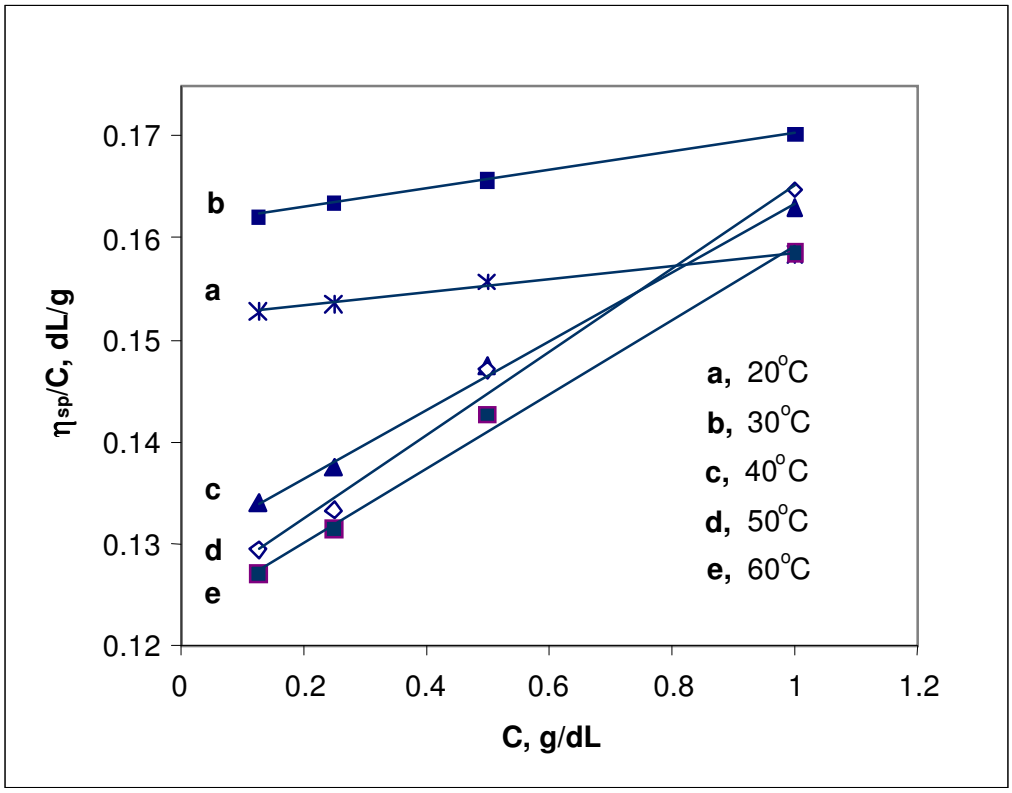


Figure 21: Dependence of viscosity behavior upon temperature of PEZ **25** (entry 2, Table 5) in 0.1 N NaCl using an Ubbelohde Viscometer.

The variation of intrinsic viscosity and Huggins parameter, k', with temperature for the PEZ **25** in 0.1 N NaCl are given in Figure 21 and Table 8. The intrinsic viscosity passes through a maximum at 30 °C and thereafter decreases with increasing temperature. Huggins parameter, which is a measure of solvent-polymer interaction, increases significantly at higher temperatures. The screening of the positive charges on the polymer chain may be altered with temperature as a result of any perturbation of the ionic atmosphere of the binding counterions of the added NaCl.

Viscosity data for the copolymer PEZ **26** (entry 1, Table 6) is presented in Figures 22 and 23. The viscosity plots ascertain the polyelectrolytic behavior of the copolymer. As in the case of the homopolymer, the intrinsic viscosity values decreases with increase in the NaCl concentration and converge to a minimum at 0.5 N NaCl; the intrinsic viscosity changes slightly there after in 1.0 and 2.0 N NaCl solution.

The variation of intrinsic viscosity and Huggins parameter, k', with temperature for the PEZ **26** in 0.1 N NaCl is given in Figure 24 and Table 8. Unlike in the case of the homopolymer, the intrinsic viscosity increases continuously with increasing temperature. An average value of 0.330 for the Huggins parameter, k', is obtained. The intrinsic viscosity in 0.5 N NaCl also increases with the increase in temperature. Which is shown in Figure 25.

TABLE 8: Dependence of the intrinsic viscosity and Huggins parameter $k^{/}$ of PEZ **(25)** and Copolymer PEZ (**26**) upon temperature for 0.1 N NaCl

Temp	Homopolymer **25**		Copolymer **26**	
	Intrinsic viscosity	$k^{/}$	Intrinsic viscosity	$k^{/}$
(^{o}C)	(dL/g)		(dL/g)	
20	0.152	0.277	0.500	0.332
30	0.161	0.346	0.556	0.251
40	0.130	1.988	0.552	0.412
50	0.124	2.656	0.602	0.326
60	0.123	2.410	0.610	0.335
70	-	-	0.621	0.328

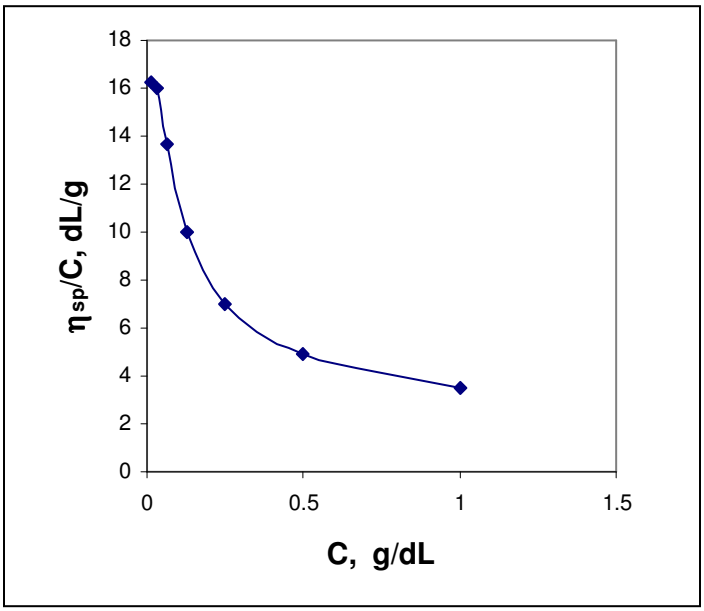


Figure 22: The viscosity behavior of PEZ **26** (entry 1, Table 6) in salt-free water at 30°C using an Ubbelohde Viscometer.

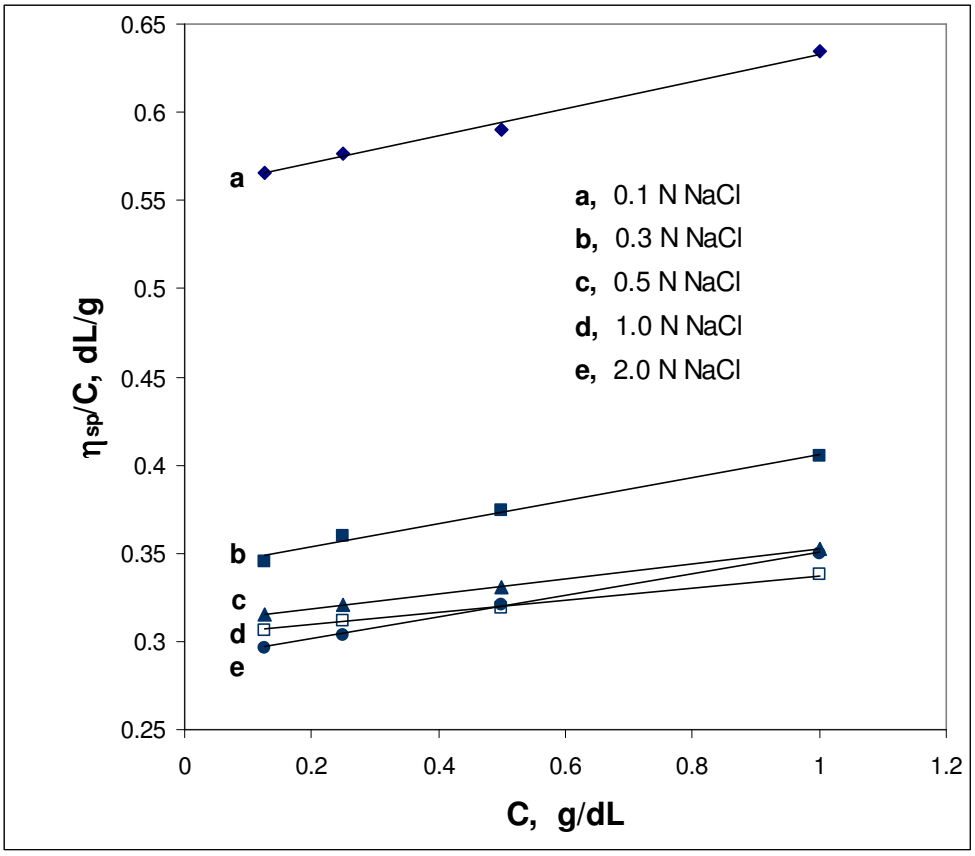


Figure 23: The viscosity behavior of PEZ **26** (entry 1, Table 6) in various NaCl solutions at 30°C using an Ubbelohde Viscometer.

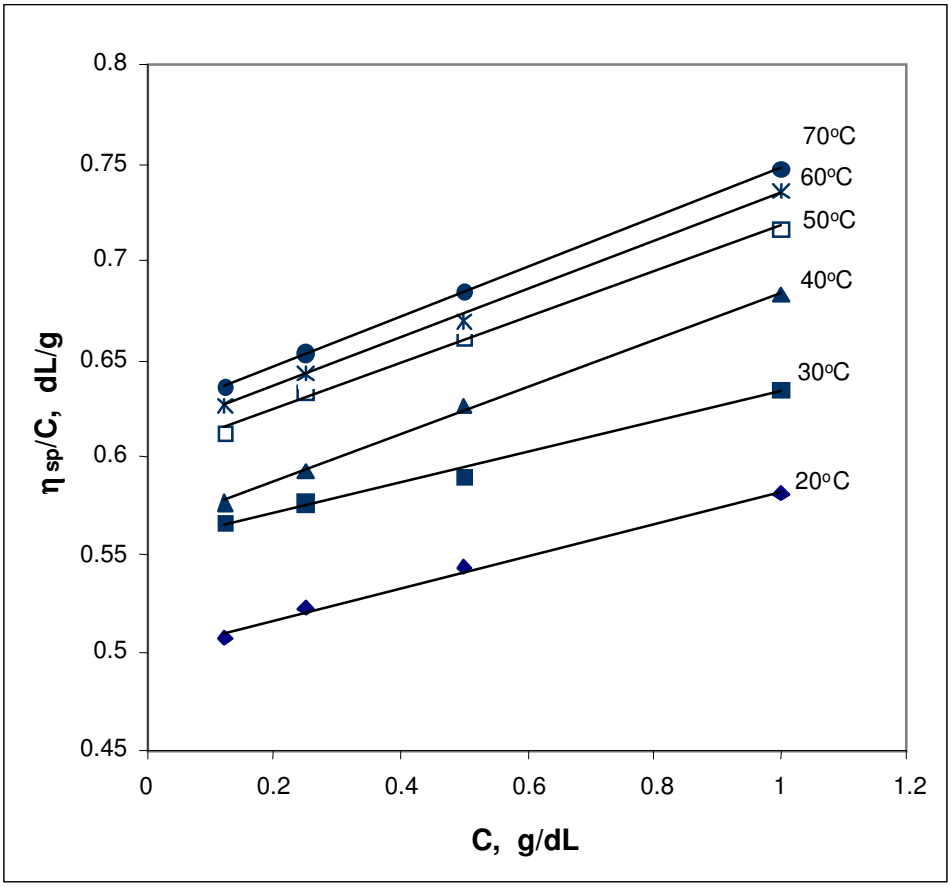


Figure 24: Dependence of viscosity behavior upon temperature of PEZ **26** (entry 1, Table 6) in 0.1 N NaCl using an Ubbelohde Viscometer.

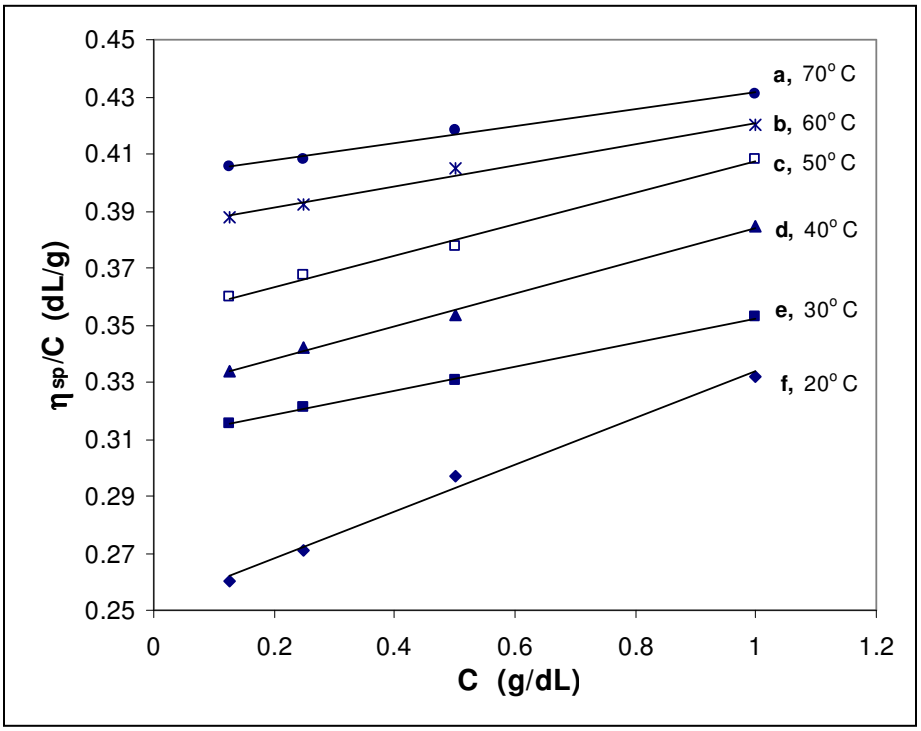


Figure 25: Dependence of viscosity behavior upon temperature of PEZ **26** (entry 1, Table 6) in 0.5 N NaCl using an Ubbelohde Viscometer.

The intrinsic viscosities of the PEZ **26** are also measured in solution containing various concentration of KI and are given in Figure 26. Polybetaine chains assume a collapsed conformation due to strong intrachain and intra-group associations, resulting from the electrostatic attractive forces between opposite charges of the zwitterionic moieties.

The iodide is among the most polarizable (soft) anion and has been shown to be extremely effective in screening the positive nitrogens on the macromolecular chain of polybetaines. Thus, the associations are disrupted and the polyzwitterions assumes an extended conformation, thereby going into solution, and the intrinsic viscosity has been found to be higher in the presence of iodide ions in compare to chlorides. But in the case of the PEZ **26**, the intrinsic viscosity values are found to be almost similar in the presence of iodide and chloride ions, thus indicating the absence of the effect of the anions on the viscosity values.

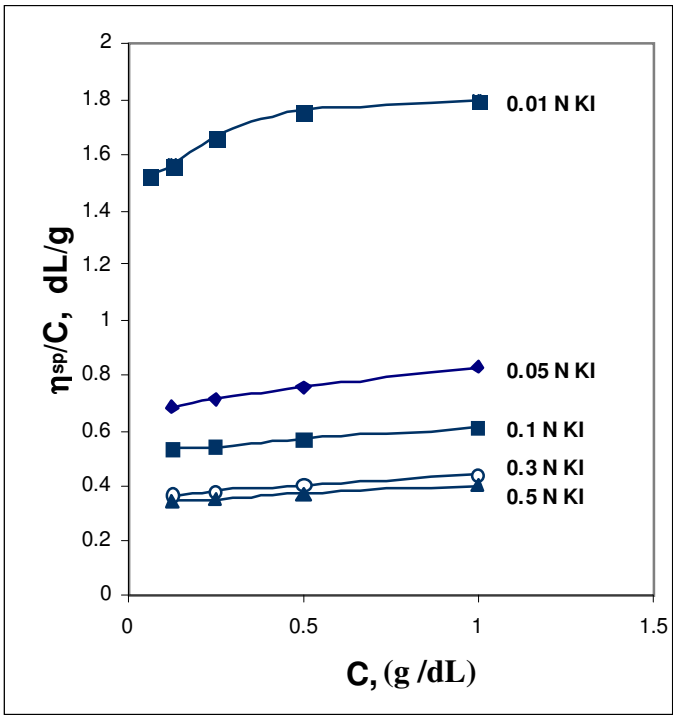


Figure 26: The viscosity behavior of PEZ **26** (entry 1, Table 6) in various KI solutions at 30^{o}C using an Ubbelohde Viscometer.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

A very convenient synthetic route for obtaining the new ionic polymers **21, 22, 25** and **26** using inexpensive starting materials has been achieved. The work described in this thesis represents the first example of a cyclopolymerization involving amine salt containing sulfobetaine moiety. The interesting pH-responsive solution properties associated with this structural feature enabled us to utilize the polysulfobetaine, for the first time, in a two-phase aqueous polymer system. Conformational behavior of the polymers is strongly influenced by the nature and the net charge on the chain. The protein's affinity toward a particular polymer phase in a two-phase system is influenced by the hydrophilicity and hydrodynamic volume of the polymer. As indicated by the viscosity and basicity constant data, the hydrophilicity and the hydrodynamic volume of the polymer APE can be controlled by the degree of protonation of the pH-responsive

amine functionality.This new ionic polymer may have applications in protein purification; its almost zero solubility in water in the absence of added salt below pH ~7 will permit its effective removal from solution by precipitation, thus leaving the protein in the solution.

4.2 RECOMMENDATIONS

1. The hydrophobic modification of these polymers can be studied.

2. The potential application of these polymers in protein separation can be analyzed.

3. The toxicity of these new polymers should be evaluated. Otherwise, this can hamper its application in the industry despite their promising features.

4. These polymers should be fully characterized using techniques such as low-angle laser light scattering technique, vapor pressure osmometry and membrane osmometry. This will provide vital information about the polymer size as well as interaction parameters between these and other polymers.

CHAPTER 5

EXPERIMENTAL

5.1 Physical Methods

Melting points were recorded in a calibrated Electrothermal IA9100 Digital melting-point apparatus at heating rates of 1 °C/min in the vicinity of melting points. Elemental analyses were carried out in a Carlo Erba model 1102 elemental analyzer. IR spectra were recorded on a Perkin Elmer 16F PC Fourier transform infrared spectrometer (spectral resolution = 4 cm^{-1}, number of scans = 19). ^{1}H and ^{13}C NMR spectra of the polymers were measured in D_2O with dioxane as an internal standard on a JEOL LA 500-MHz spectrometer. Viscosity measurements were made with an Ubbelohde viscometer (viscometer constant = 0.005718 cSt/s at all temperatures) using CO_2-free water under N_2 to avoid CO_2 absorption, which may affect the viscosity data. A gentle stream of N_2 was passed through distilled deionized water at 90^{o}C for 15 min in order to remove dissolved gases. This water was used in viscosity measurements.

5.2 Materials

t-Butylhydroperoxide (80% in ditertiarybutylperoxide), diallylamine and 1,3-propanesultone from Fluka Chemie AG (Buchs, Switzerland) were used as received. AIBN from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from a chloroform-ethanol mixture. Acetonitrile (HPLC Grade) was dried over Linde 4A molecular sieves. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64-65°C (4 mmHg). All glassware was cleaned with deionized water. For dialysis, a Spectra/Pore membrane with a molecular weight cut-off (MWCO) value of 6-8000 was purchased from Spectrum Laboratories, Inc. Poly(ethylene glycol) (PEG) with a molecular weight of 35,000 was purchased from Merck-Schuchardt.

5.3 Sodium 3-(*N, N*-diallylamino) Propanesulfonate (19)

A solution of diallylamine **17** (49.6 g, 98% pure, 0.500 mol) and 1,3-propanesultone (28.3 g, 98% pure, 0.227 mol) in acetonitrile (65 cm^3) was stirred under N_2 at 40 ºC for 24 h. The solvent and the excess diallylamine were removed by a gentle stream of N_2 at 60 ºC. The residual mixture was treated with 1 N NaOH solution (235 cm^3, 0.235 mol), and was extracted with ether (3x100 cm^3) to remove the excess diallylamine. The sodium salt of the monomer **19** was recovered from the aqueous layer by freeze-drying followed by crystallization from methanol/acetone mixture as white crystals (49.4 g, 90.2%). The melting point was 125-127 °C (closed capillary).

ELEM. ANAL. Calcd. for $C_9H_{16}NO_3SNa$: C, 44.80%; H, 6.68%; N, 5.81%; S, 13.29%. Found: C, 44.5%; H, 7.09%; N, 5.67%; S, 13.09%.

ν_{max} (KBr): 3625 (w), 3452 (w), 3078, 3006, 2976, 2932, 2806, 1644, 1450, 1420, 1354, 1262, 1194 (broad), 1148, 1110, 1056, 994, 950, 918, 842, 792, 736, 620 cm^{-1}.

δ_H (D_2O): 1.79 (2 H, quint, *J* = 7.9 Hz), 2.47 (2 H, t, *J* = 7.9 Hz), 2.73 (2 H, t, *J* = 7.9 Hz), 3.02 (4 H, d, *J* = 6.8 Hz), 5.13 (4 H, m), 5.75 (2 H, m), (HOD: 4.65).

δ_C (D_2O): 21.51, 49.93, 51.66, 56.58, 120.16 (CH_2, t, by undecoupled spectra; Figure 3), 134.44 (CH, d, by undecoupled spectra; Figure 3) (dioxane, 67.40 ppm).

5.4 3-(*N, N*-diallylammonio) Propanesulfonate (20)

A solution of the sodium salt **19** (44.6 g, 0.185 mol) in water (55 cm^3) was stirred with Dowex 50Wx8 (78 g) at room temperature for 1 h. The aqueous solution becomes acidic as indicated by litmus test. The solution was filtered through a cotton bed in a column and the resin was thoroughly washed by passing deionized water (150 cm^3) through it. The zwitterionic monomer was recovered by freeze-drying. The thick liquid was then dried to a constant weight *in vacuo* at 65 °C to obtain 38.5 g (95 %) of the sulfobetaine (SB) monomer **20** as a light yellow thick liquid.

ν_{max} (neat): 3448, 3000, 2672 (broad), 1462, 1212 (broad), 1164, 1036, 952, 784, 730 cm^{-1}.

δ_H (D_2O): 2.10 (2 H, quint, *J* = 8.0 Hz), 2.89 (2 H, t, *J* = 7.3 Hz), 3.23 (2 H, t, *J* = 8.1 Hz), 3.73 (4 H, d, *J* = 7.3 Hz), 5.53 (4 H, m), 5.85 (2 H, m), (HOD: 4.65).

δ_C (D_2O): 20.17, 48.45, 51.38, 55.70, 126.18, 127.61 (dioxane, 67.40 ppm).

5.5 Sodium N- (3-sulfopropyl)-3-(N, N diallyl amino) Propane Sulfonate (24)

A mixture containing the sodium 3-(*N, N*-diallylamino) propanesulfonate **23** (25 g, 104 mmol) and 1,3-propanesultone (25 g, 205 mmol) in dry acetonitrile (500 cm^3) was stirred at 70°C in a closed vessel for 48 h. The sodium salt was partially soluble in the mixture and the reaction proceeded then a clear solution was obtained within 6 h. Continued reaction resulted in the formation of more product which settled as a thick liquid at the bottom of the flask. At the end of the elapsed time, the mixture was concentrated to an approximate volume of 100 cm^3. The supernatant liquid was decanted, and the thick liquid was dissolved in methanol (50 cm^3) and precipitated in acetone (250 cm^3). The process was repeated thrice to obtain the electrolyte-zwitterionic monomer **24** as a highly hygroscopic white solid, which was dried to a constant weight (29.9 g, 79.2%) at 60 °C under vacuum. The melting point was 202-207 ^oC (closed capillary).

ν_{max} (KBr): 3447(s), 2971, 1647, 1545, 1475, 1424, 1364, 1194 (s), 1047, 961, 736 cm^{-1};

δ_H (D_2O): 2.12 (4 H, quint, *J* = 7.9 Hz), 2.85 (4 H, t, *J* = 7.1 Hz), 3.31 (4 H, apparent t, *J* = 8.6 Hz), 3.85 (4 H, d, *J* = 7.4 Hz), 5.62 (4 H, m), 5.91 (2 H, m), (HOD: 4.65).

δ_C (D_2O): 18.26, 47.99, 57.30, 61.68, 124.42, 129.82 (dioxane, 67.40 ppm).

5.6 General Procedure for the Polymerization of (20)

All the polymerizations were carried out under the conditions described in Table 1**.** The experiment under entry 16 was repeated on a large scale as described next. A solution of the monomer **20** (10.5 g, 47.9 mmol) and NaCl (72 mg) in CO_2 and O_2 free deionized water (3.5 g) in a 10 cm^3 round bottomed flask was purged with N_2, and after adding the required amount of the initiator (22.5 mg), the mixture was stirred in the closed flask at 80 ^oC for 24 h followed by 90 °C for another 24 h. The reaction mixture remained transparent throughout the process. At the end of the specified time, the ^1H NMR spectra of the crude reaction mixture revealed the composition of the polysulfobetaine (PSB) **21** and unreacted monomer **20**. The reaction mixture was cooled, dissolved in a minimum amount of 1 N NaCl, transferred to a dialysis bag and dialyzed against deionized water for 24 h for the removal of the unreacted monomer and the added salt (NaCl) (checked with $AgNO_3$ test). Within an hour, the polymer started separating out of the solution. The dialysis was continued for an additional 72 h. The separated polymer was then dried at 70 °C *in vacuo*, and then crushed into powder and redried to a constant weight at 70 °C to obtain the PSB **21** (7.95 g, 75.7 %) as a white polymer.

Onset of thermal decomposition (closed capillary): the color changed to brownish black at 275 °C, but the polymer did not melt or char up to 400 °C.

ELEM. ANAL. Calcd. for $C_9H_{17}NO_3S$: C, 49.29%; H, 7.81%; N, 6.39%; S, 14.62%. Found: C, 48.7%; H, 8.25%; N, 6.25%; S, 14.6%.

ν_{max} (KBr): 3458, 2932, 2742, 1654, 1466, 1204 (broad), 1038, 734 cm^{-1}.

5.7 Conversion of the Polysulfobetaine (PSB) 21 to Anionic Polyelectrolyte (APE) 22

The PSB **21** (0.877 g, 4.0 mmol) was treated with 2 N NaOH (3.0 cm^3) at 20 °C for 5 min, and the resulting APE **22** was precipitated into acetone (25 cm^3). The polymer was redissolved in water (1 cm^3), and reprecipitated in acetone (25 cm^3). The polymer was then soaked in methanol for 12 h, and then dried at 70 °C *in vacuo* to a constant weight (0.782 g, 81 %).

Onset of thermal decomposition (closed capillary): the color changed to blackish brown at 350 °C, but the polymer did not melt or char up to 400 °C.

ELEM. ANAL. Calcd. for $C_9H_{16}NNaO_3S.H_2O$: C, 41.69%; H, 7.00%; N, 5.40%; S, 12.36%. Found: C, 41.5%; H, 7.3%; N, 5.25%; S, 12.0%.

ν_{max} (KBr): 3456, 2926, 2854, 2800, 1656, 1458, 1200 (broad), 1050, 798, 738 cm^{-1}.

5.8 General Procedure for the Homopolymerization of the Monomer (24)

All the polymerizations were carried out under the conditions described in Table 5**.** The experiment under entry 2 was repeated on a large scale as described next. A solution of the monomer **24** in CO_2 and O_2 free deionized water in a 10 cm^3 round bottomed flask was purged with N_2, and after adding the initiator the mixture was stirred in the closed flask at 70 ^oC for 20 h followed by 80 ^oC for another 20 h. The reaction mixture remained transparent throughout the process. At the end of the specified time,

the ^{1}H NMR spectra of the crude reaction mixture revealed the composition of the PEZ **25** and the unreacted monomer **24**. The reaction mixture was cooled, and transferred to a dialysis bag and dialyzed against deionized water for 24 h for the removal of the unreacted monomer. The polymer solution was then freeze-dried and subsequently dried to a constant weight at 70^{o}C under vacuum. The hygroscopic white polymer was then kept in a desiccator.

Onset of thermal decomposition (closed capillary): the color changed to brownish black at 340 ^{o}C, and black at 400 ^{o}C.

ν_{max} (KBr): 3443 (s), 2923, 1653, 1461, 1191 (s), 1048 (s), 737, 601 cm^{-1}.

5.9 General procedure for the Copolymerization of the Monomer 24 with SO_2

All the polymerizations were carried out using conditions as described in Table 6. The experiment under entry 1 was repeated on a large scale as described next. In a typical experiment, required amount of SO_2 was absorbed in a solution of the monomer **24** in DMSO. The required amount of the initiator (AIBN) was then added under N_2 and the closed flask was stirred using magnetic stir-bar at 57^{o}C for 24 h. Within hours, the magnetic bar stopped stirring and finally the reaction mixture became cloudy. At the end of the elapsed time, the mixture was soaked in methanol, filtered and washed with liberal excess of hot (50^{o}C) methanol to ensure the complete removal of the unreacted monomer (as indicated by ^{1}H NMR). The copolymer was then dried to a constant weight at 55 ^{o}C under vacuum. The white copolymer PEZ **26,** was stored in a desiccator.

The onset of thermal decomposition (Closed capillary): the color suddenly changed to black at 320^{o}C.

ν_{max} (KBr) 3444 (s), 2961, 2923, 1646, 1464, 1418, 1308, 1188 (s), 1132, 1046, 928, 860, 796, and 736 cm^{-1}.

5.10 Solubility Measurements and Cloud Point Titrations in Aqueous Salt Solutions

Solubility of the PSB **21**, APE **22,** PEZ **25** and Copolymer PEZ **26** in organic solvents at room temperature was established for 2% wt/wt solutions, after preheating at 70 °C for 1 h. The Critical (minimum) Salt Concentration (CSC) required to promote water solubility at 23 °C was measured by titration of 1% w/w polymer solution at sufficiently high salt concentration with deionized water. The accuracy of the CSC values, obtained by visual determination of the first cloud point, was approximately ±1-2%. The results of the solubility are given in Tables 2 and 7, respectively. The result of CSC for aqueous solutions of PSB **23** is depicted in Table 3.

5.11 Potentiometric Titrations

The potentiometric titrations were carried out at 25 °C. A gentle stream of N_2 was passed through distilled and deionized water at 90 °C for 15 min for the removal of dissolved gases. This water was used for titration in salt-free and salt (NaCl, 99.9% purity) solutions and for viscosity measurements. For each titration, 200 cm^3 of a salt-

free or 0.1 N NaCl solution containing a weighed amount (usually ca. 0.40-0.63 mmol) of the anionic monomer **19**, PSB **21** (or APE **22**) was used. In the case of PSB, the polymer was first dissolved in one equivalent of 0.1046 N NaOH, and then diluted to the required volume. The solution was titrated at 25 °C with 0.1015 M HCl delivered by a burette under N_2. After each addition of the titrant (0.25 cm^3), the solution was stirred briefly with a magnetic stir bar under N_2. The pH of the solution was recorded with a Corning 220 pH meter. Under the conditions (including a large volume of 0.1 N NaCl), the small amount of polymers or the small volume of the titrant used did not contribute much to the ionic strength, and as such, the data were not corrected to zero ionic strength and the activity coefficient corrections were not applied.

The protonation constant of the amine nitrogen, log *K,* was calculated at each pH value by the well-known Henderson-Hasselbalch equation (eq 1), where the degree of protonation (α) is the ratio $[ZH^{\pm}]_{eq}/[Z]_o$. The $[Z]_o$ is the initial analytical concentration of the monomeric units in the APE **22** (or PSB **21**), and $[ZH^{\pm}]_{eq}$ is the concentration of the protonated species at the equilibrium given by $[ZH^{\pm}]_{eq} = C_{H}^{+} - [H^{+}] + [OH^{-}]$, where C_{H}^{+} is the concentration of the added HCl; $[H^{+}]$ and $[OH^{-}]$ at equilibrium were calculated from the pH value [93]. The typical electrolytes having apparent basicity constants could be described by eq 2, where log K^o is the pH at $\alpha = 0.5$ and $n = 1$ in the case of sharp basicity constants. The linear regression fit of pH versus log $[(1-\alpha)/\alpha)]$ gave log K^o and n as the intercept and slope, respectively. The experimental details of the potentiometric titrations are summarized in Table 4.

5.12 Viscometric Titration

The viscometric titration was performed at 25 °C in the presence of various amounts of HCl, but the concentration of the polymer was kept constant throughout. Two stock solutions of 0.02280 M (#A) and 2 x 0.02280 M (#B) polymer APE **22** were prepared in 0.1 and 0.2 N NaCl, respectively, (the stock #A contained 0.5 g/dL of the PSB **21** neutralized with one equivalent of NaOH**)**. The reduced viscosity and pH of the 0.02280 M stock solution were measured. A known volume (usually about 0.4-0.7 ml) each of a 0.1015 N HCl and the stock solution #B was added to a known weight or volume (~20 ml) of the stock solution #A in an Erlenmeyer flask Equal volumes of HCl solution and stock #B (having twice the molarity of the stock #A) were added to the stock #A to keep the concentrations of NaCl and the polymer unchanged. The reduced viscosity and pH of the new solution A_1 were measured. The results described the representing system is depicted in Table 9. The solution was then returned to the original Erlenmeyer flask, and its weight was noted. Again, an equal volume of #B and 0.1015 N HCl were added to the known weight of the A_1. The pH and viscosity of the new solution A_2 were measured.

TABLE 9: Viscometric Titration Behaviour in Presence of Various Amount of HCl at 25 °C

Entry no.	Viscosity Z^-	Z^- [a] (Mole)	HCl[b] equiv (Each entry)	HCl equiv (Combined)	Red. Visco[c]. (dL/g)	pH	log (1-α)/ α = (pH-logk^o)/n[e]	α[d]	$ZH^{\pm}$ (% of α)	Z^- (% of 1-α)	$ZH^{\pm}$ (100%=0.7) Red. Visco.	Z^- Red. Visco.
1	212.95	0.0228	0	0	0.6586	11.44	1.0331	0.0848	8.48	91.52	0.0594	0.6406
2	210.90	0.0228	0.0021	0.0936	0.6330	11.11	0.8146	0.1329	13.29	86.71	0.0930	0.6070
3	208.30	0.0228	0.0048	0.2104	0.6005	10.75	0.5762	0.2097	20.97	79.03	0.1468	0.5532
4	205.35	0.0228	0.0074	0.3245	0.5637	10.40	0.3444	0.3115	31.15	68.85	0.2181	0.4819
5	198.20	0.0228	0.0108	0.4752	0.4744	9.89	0.00662	0.4962	49.62	50.38	0.3473	0.3527
6	187.25	0.0228	0.0140	0.6129	0.3377	9.52	-0.2384	0.6339	63.39	36.61	0.4437	0.2563
7	172.75	0.0228	0.0169	0.7404	0.1567	9.22	-0.4371	0.7323	73.23	26.77	0.5126	0.1874
8	167.95	0.0228	0.0177	0.7749	0.0967	9.08	-0.5298	0.7720	77.20	22.80	0.5404	0.1596

[a]0.4469 mmol 0f PSB **21** neutralized with 1 equivalent of NaOH then diluted to 19.6 cm^3 by adding 0.1N NaCl to make the 0.02280M stock solution **A** with concentration 0.5 gm/dL.

[b]All cases equal quantity of stock **B** solution was added with required quantity of HCl to keep concentration of the polymer and NaCl unchanged. 0.4240 mmol 0f PSB **21** neutralized with 1 equivalent of NaOH then diluted to 9.3 cm^3 by adding 0.2N NaCl to make the 0.04560M stock solution **B** with concentration 1.0 gm/DL.

[c]Reduced viscosity = η_{sp}/c.

[d]α is the degree of protonation.

[e]logk^0 and n is determined from Figure 18(b).

The dilution changes the mole equivalent of the added HCl, and its amount should be recalculated. Each time, the viscometer is cleaned and dried. Similar dilutions were done to obtain pH and reduced viscosity values of the 0.02280 M polymer solution in the presence of different amounts of added HCl, the range of which is shown in Figure 16. Pure CO_2-free water was used throughout, and the solutions were used immediately after preparation. A gentle stream of N_2 was passed over the open arms of the viscometer to prevent carbon dioxide absorption. The percentage of different ionic species in the solutions was calculated using eq 2.

5.13 Phase Compositions and Phase Diagram

Stock Solution (A) 25 w/w % (PSB: APE):

1.68 gm (7.66 mmol) of **PSB 21** in deionized water (5.0 cm^3) was treated with 0.60 equivalent [184.0 mg (4.6 mmol)] of NaOH.To the resulting solution containing 40:60, PSB/APE was added 37.2 mg KCl to make the solution 25 w/w % in original PSB and 0.1 N KCl (total weight of the mixture 6.73 gm).

Stock Solution (B) 25%w/w PEG:

2.04 gm (46.2 mmol) of PEG 35,000 was dissolved in deionized water (6.0 cm^3) and add 44.8 mg of KCl to make the 25%w/w PEG stock solution in 0.1 N KCl.

The following Stock Solutions are used to determine the Phase Composition and construct the Phase Diagram by **NMR** and **Turbidity** method.

(I) NMR Method

To a mixture of 147.6 mg (0.5906 gm of stock solution B) of PEG-35000 and 157.3 mg (0.6294 gm of stock solution A) of PSB **21** (Entry A, Table 10) was added 0.5299 gm of water. The mixture was shaken to complete the solution process. The phase separation happened within minutes after thorough shaking, and the mixture was kept at 23 °C for 24 h. The volume of the top and bottom layers was found to be 0.7947 and 0.8514 cm^3, respectively. Density of the top and bottom layer was determined to be 1.0473 and 1.0777 gcm^{-3}, respectively. The ^1H NMR spectra of the top and bottom layers were measured in D_2O (after removal of H_2O by a gentle stream of nitrogen and repeating the process after adding some D_2O to the residue). The top and bottom layers were found to be overwhelmingly rich in PEG and PSB, respectively. The top layer was found to contain $(PEG/PSB)_{top}$ in a respective ratio of 150/1 and that of the bottom layer 0.25/1.69, respectively.

Weight percent of each polymer is determined by using the equations

$$[PSB_t]V_t + [PSB_b]V_b = PSB_o / MM_{PSB} \quad (4)$$

$$[PSB_t]V_t ([PEG] / [PSB])_t + [PSB_b]V_b ([PEG] / [PSB])_b = PEG_o / MM_{PEG} \quad (5)$$

Where, subscript t and b represent top and bottom phase, respectively. [PSB] and [PEG] represent concentration of the polysulfobetaine and poly(ethylene glycol) in mmol of repeat unit cm^{-3}.

TABLE 10: Phase Composition of the PSB **21** – PEG 35,000 - H_2O System in 0.1N KCl at 23 °C

System	Total system		Top phase			Bottom phase			
	PSB (%w/w)	PEG (%w/w)	PSB (%w/w)	PEG (%w/w)	d[b] top	PSB (%w/w)	PEG (%w/w)	d[b] bottom	Volume ratio[a]
A	8.9919	8.4376	0.5711	17.198	1.0473	16.629	0.4915	1.0777	0.933:1
B	5.5701	8.4136	0.5529	12.899	1.045	14.354	0.7661	1.0683	1.786:1
C	6.4426	5.5018	0.5139	10.318	1.0464	12.258	0.7776	1.0669	001:001
D	4.2701	7.1136	0.5029	10.099	1.0487	12.154	0.8661	1.0689	2.133:1
E	6.2575	4.2218	0.4091	8.2144	1.0498	10.759	1.1489	1.0656	0.781:1

[a]volume ratio of top and bottom phase.

[b]density of the top and bottom phase.

PSB_o and PEG_o represent total mass in mg of the polymers and V represent the volume in cm^3. MM_{PSB} and MM_{PEG} represent molar masses of the repeat units of the PSB and PEG were taken as 219.3 and 44.03, respectively. [PEG]/[PSB] represents molar ratio of the polymers as determined by ^1H NMR integration. After multiplying equation (4) with $(PEG/PSB)_t$ and then subtracting from equation (5) , a simple rearrangements leads to

$$[PSB_b] = \frac{PEG_o/44.03 - (PSB_o/219.3)([PEG]/[PSB])_t}{V_b\{([PEG]/[PSB])_b - ([PEG]/[PSB])_t\}} \quad (6)$$

The mass of polymer PSB in the bottom phase is then calculated using

$$PSB_b = [PSB_b]V_b \text{ x } 219.3 \text{ mg.} \quad (7)$$

Once one of the polymer concentrations is known in a phase, then the rest of the concentrations and weight percents of the polymers in the two phases are easily calculated from the known volume, density and mass of the two phases.

For instance, if the total system represented by the point A, will have the volume or mass ratio of the top and bottom phases determined by the ratio of length $A - A_{bot}$ and $A - A_{top}$, respectively.

The results just described represent system A in Table 10. Likewise several other systems of known compositions of PEG-35, 000 and PSB **21** in 0.1 N KCl as described in Table 10 and 11 (as represented by points A- D, E in Fig. 17) was made.

In the presence of PSB and APE (since the mixture contained a 40:60 mixture of the ionic polymers), the determination of the mole ratios were difficult because the singlet for PEG at δ 3.58 overlapped with the signals for the PSB protons which were shifted downfield. However, basification (K_2CO_3) leading to the APE followed by ^1H NMR measurements allowed us to determine the mole ratios.

The ^1H NMR signals for the polymers were well separated in the absence of HCl, and the mole ratios of the repeating units of the polymers were easily calculated using the integration of the four-proton singlet at δ 3.58 for PEG and the sixteen-proton complex signals in the range δ 0.75-3.10 for the polymer APE. The tie lines A-E were constructed using the wt% of the polymers in the top, bottom and total systems (Table 10).

TABLE 11: Phase Behaviour of PEG 35,000 and PSB **21** at 23 °C.

Data Points	Stock A (gm)	Stock B (gm)	ZH±, Z-a (gm)	PEG (gm)	PEG-tot (gm)	Total (gm)	%ZH±, Z- (%w/w)	%PEG (%w/w)
1	1.4614	0.0648	0.36535	0.01620	0.0162	3.044	12.004	0.5323
2	1.4614	0.0524	0.36535	0.01310	0.0293	3.566	10.244	0.8215
3	1.4614	0.0642	0.36535	0.01605	0.0454	4.162	8.778	1.0896
4	1.4614	0.1028	0.36535	0.02570	0.0711	4.778	7.644	1.4865
5	1.4614	0.1218	0.36535	0.03045	0.1015	5.378	6.792	1.8868
6	1.4614	0.1358	0.36535	0.03395	0.1355	5.942	6.149	2.2796
7	1.4614	0.1822	0.36535	0.04555	0.1810	6.788	5.383	2.6668
8	1.4614	0.2484	0.36535	0.06210	0.2431	7.744	4.718	3.1396
9	1.4614	0.2328	0.36535	0.05820	0.3013	8.750	4.176	3.4435
10	1.4614	0.3558	0.36535	0.08895	0.3903	10.134	3.605	3.8508
11	1.4614	0.3586	0.36535	0.08965	0.4799	11.522	3.171	4.1653
12	1.4614	0.4166	0.36535	0.10415	0.5841	13.108	2.787	4.4556
13	1.4614	0.5594	0.36535	0.13985	0.7239	15.212	2.402	4.7585
14	1.4614	0.593	0.36535	0.14825	0.8722	17.334	2.108	5.0317
15	1.4614	0.6762	0.36535	0.16905	1.0412	19.678	1.856	5.2909
16	1.4614	0.7974	0.36535	0.19935	1.2406	22.212	1.645	5.5847
17	1.4614	0.762	0.36535	0.19050	1.4311	24.906	1.467	5.7459

Stock Solution A: 25 %w/w (PSB: APE;; 40:60).

Stock Solution B: 25 %w/w PEG.

(II) Turbidity Method

1.46 g of a concentrated solution (25 %w/w) of PSB (treated with 0.60 equiv NaOH) [Stock Solution A] in 0.1 N KCl was taken in a flask and titrated with a concentrated solution (25 %w/w) of the PEG (in 0.1 N KCl) [Stock Solution B] of molecular weight 35,000 and stirred with a magnetic stir bar until the transparent system turned turbid. Then, a known weight of 0.1N KCl solution was added drop wise until the system became transparent again. At this point, the final composition of the two polymers calculated corresponds to a point on the binodial curve. After obtaining the first point, a concentrated solution of PEG was added again to obtain a turbid suspension, and dilution with water (0.1N KCl) was repeated to obtain a second point on the binodial. This procedure was continued until a sufficient number of points for the construction of the binodial curve were obtained. Points obtained by turbidity method are shown in Table 11 and are joined together in Figure 17. The experiments were carried out at 23 °C.

NOMENCLATURE

cm	Centimeter
ppm	Parts Per Million
ε	Dielectric Constant
η	Intrinsic Viscosity.
η_r	Relative Viscosity
η_{sp}	Specific Viscosity
C	Concentration
Hz	Hertz
°C	Degree Celsius
δ	Chemical Shift
K	Protonation Constant
α	Degree of Protonation
V	Volume
R^2	Correlation Coefficient
K'	Huggins Parameter

REFERENCES

1. M.F. Hoover and H.E. Carr, *J.Tech. Assoc. Pulp Paper Ind*, **51**, 556 (1968)
2. G.B.Butler, *Acc.Chem.Res*, **15**, 370 (1982)
3. R.M. Ottenbrite and W.S.Ryan *Jr. Ind Eng. Chem. Prod. Res. Develop*, **19**, 528 (1982).
4. D.Hunkeler, A.E.Hamielec, and W.Baade, *Adv. Chem. Series*, **223**, 176 (1989)
5. C. L. McCormick, *J. Polym Sci,* **34**, 911 (1996).
6. J. Lancester, L. Baccei, and H. Panzer, *J.Polym. Sci. Polym. Lett. Edn*.**14**, 549 (1976).
7. *Chemical Economics Handbook*, Stanford Research Institute Menlo Park, Ca, PP 581-10111,581-50222,581- 1012D (1983).
8. R. M. Ottenbrite, and W. S. Ryan, *Jr. ind. Eng. Chem. Prod. Res. Develop*, **19**, 528 (1980).
9. C.F.Carlson, *U.S.Pat. 2*, **297**, 691 (Oct.1942); and *U.S. Pat. 2*, **357**, 809 (Sept 11, 1944).
10. G.B.Butler and R.L.Bunch, J.Am.Chem.Soc., 71, 3120 (1949).

11. G. B. Butler, *Acc. Chem. Res*., **15**, 370 (1982).

12. G. B. Butler, F. L. Ingley, *J. Am. Chem. Soc*. **73**, 895 (1951),

13. G. B. Butler, *J. Polym. Sci.* **34**, 913 (1996).

14. G. B. Butler, Cyclopolymerization and Cyclocopolymerization.New York: *Marcel Dekker*, (1992).

15. S. R. Johns, R. I. Willing, S. Middleton, and A. K. Ong*, J. Macromol.Sci.Chem.A* , **10,** 875 (1976).

16. S. Harada, and M. Katayama, *Makromol.Chem.* **90**, 177 (1966).

17. S. Harada, K. Arai, *Makromol Chem*. **64,** 107 (1967).

18. S. A. Ali, S. Z. Ahmed, M. I. M. Wazeer, E. Z. Hamad, *Polymer*, **38**, 3385 (1997).

19. S.Harada and M.Katayama, *Makromol.Chem*, **90,** 127 (1963).

20. D. E. Weiss, B. A. Bolto, R. Mc Neill, A. S. McPherson, R. Siudak, E. A. Swinton and D Willis, *Aust.J.Chem*, **19,** 561, 589, 765, 791 (1966).

21. A.L.Clingman, J.R.Parrish and R.Stevenson, *J.Appl. Chem*. **13**, 1 (1963).

22. P. Anton, A. Laschewsky, *Makromol Chem.* **194**, 601 (1993).

23. T. A. Wielema, J. B. F. N. Engberts, *Eur Polym J*, **23**, 947 (1987).

24. J. J. Kaladas, R. Kastrup, D. N. Schulz, *Polym Prepr.* **39(1),** 619 (1998).

25. D. B. Thomas, R. S. Armentrout, C. L. McCormick, *Polym Prepr*. **40(2**), 275 (1999).

26. R. S. Armentrout, C. L. McCormick, *Polym Prepr*. **40**, 193 (1999).

27. S. A. Ali, A. Rasheed, M. I. M. Wazeer, *Polyme,* **40**, 2439 (1999).

28. S. A. Ali, A. Rasheed, *Polymer,* **40**, 6849 (1999).

29. M. M. Ali, H. P. Perzanowski, S. A. Ali, *Polymer,* **41**, 5591 (2000).

30. P. S. Mumick, P. M. Welch, Z. S. Salazar, C. L. McCormick, *Macromolecule,* **27**, 323 (1994).

31. D. Srivastava, M. Muthukumar, *Macromolecule,* **29**, 2324 (1996).

32. A. Sali, E. Shaknvich, M. Kanplus, *Nature,* **369**, 248 (1994).

33. P. G. Wolynes, J. N. Onuchic, D. Thirumalai, *Science,* **267**, 1619 (1995).

34. T.A. Wielama, and J.B.F.N. Engberts, *Eur. Poly J*. **23**, 947 (1987).

35. J. C. Salamone, W. Volksen, A. P. Olson, S. C. Israel, *Polymer,* **19**, 1157 (1978).

36. V. M. Monroy Soto, J. C. Galin, *Polymer,* **25**, 254 (1984).

37. D. N. Schultz, D. G. Peiffer, P. K. Agarwal, J. Larabee, J. J. Kaladas, L. Soni, H. Handwerker, R. T. Gardner, *Polymer,* **27**, 1734 (1986).

38. M. Skouri, J. P. Munch, S. J. Candau, S. Nyret, F. Candau, *Macromolecules,* **27**, 69 (1994).

39. P. G. Higgs, J. F. Joany, *J. Chem. Phys.* **94**, 1543 (1991).

40. S. Gopal Krishnan, G. B. Butler, T. E. Hogen - Esch, and N. Z. Zhang, in "Water Soluble Polymers" Ed. S.W.Shalaby, C.L. McCormick and G.B. Butler, *ACS Symposium Series,* **467**, Ch.11, P175 (1991).

41. Y. Chang, and C. L. McCormick, *Polymer*, 35, 3503 (1994).

42. C. H. Do, and G. B. Butler, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem*. **30(2),** 352 (1989).

43. Y. J. Yang, and J. F. B. N. Engberts, *Rec. Tray. Chim, Pays-Bas*, **110 – 384** (1991)**.**

44. Y. J. Yang, J. F. B. N. Engberts, *J. Org. Chem*. 4300 (1991).

45. S. A. Ali, S. Z. Ahmed, and E. Z. Hamad, *J. Appl. Poly Sci*. **61**, 1077 (1996).

46. S. A. Ali, S. Z. Ahmed, M. I. M. Wazeer, E. Z. Hamad, *Polymer*, **38**, 3385 (1997).

47. S. A. Ali, M. I. M. Wazeer, and S. Z. Ahmed, *J. Appl. Poly. Sci*. accepted.

48. S. A. Ali, Aal-e-Ali, *Polymer*, **42**, 7961 (2001).

49. H. A. Al-Muallem, M. I. M. Wazeer, S. A. Ali, *Polymer,* **43**,1041 (2002).

50. S. A. Ali, H. A. Al-Muallem, M. I. M. Wazeer, *J. Pol. Sci., Part A, Polymer Chem*. **40,** 2464 (2002).

51. H. A. Al-Muallem, M. I. M. Wazeer, S. A. Ali, *Polymer*, **43**, 4285 (2002).

52. P. Albertsson. *Partition of Cell particles and Macromolecules*, 3rd Ed. Wiley, N.Y., (1986)

53. M. R. Kula, K. H. Kroner, H. Hustedt, *Adv. Biochem. Eng.* **24**, 73 (1982).

54. F. Hachem, B. A. Andrews, J. A. Asenjo, *Ennzyme Microb Technol.* **19**, 507 (1996).

55. M. Lu, F. J. Tjerneld, *Chromat A*. 766 (1997).

56. H.Staudinger and W.Heuer.*Ber*, **67,** 1164, (1934).

57. Butler, Bunch, *J. Am. Chem. Soc*, **71,** 320 (1949).

58. G.B.Butler, A.Crwshaw, and W.W.Miller, *J. Am. Chem. Soc*, **80**, 3615 (1958).

59. P. J. Flory, *J. Am. Chem. Soc***, 59**, 241 (1937).

60. G. B. Butler in "Polymeric Amines and Ammonium Salts", E.J. *Goethe's, Ed, Pergamon Press, New York,* PP 125-161(1981)

61. T. Kodaira and F. Aoyama, *J. Polm. Sci. Polym. Chem. Ed*, **12**, 897 (1974).

62. T. Kodaira, M. Ni-imoto and F. Aoyama, *Macromol. Chem.* **179**, 1791 (1978).

63. T. Kodaira and M. Sakai, *Polym .J,* **11**, 595 (1979).

64. D. G. Hawthorne, S. R. Johns, D. H. Solomon and R. I. Willing, J.Chem. Soc., Chem. Commun, 982 (1975); *Aust. J. chem.,* **29**,1955 (1976).

65. A. L. J. Beckwith, *Tetrahedron*, **37**, 3073 (1981).

66. G. B. Butler and R. L. Goette, *J. Am. Chem. Soc*, **74**, 1939 (1952).

67. D. H. Solomon and D. G. Hawthrone, *J. Macromol. Sci. Rev. Macromol. Chem*., **C15 (1)**, 143 (1976) and references cited therein.

68. G. B. Butler, *U.S.Patent 3*, **288**, 770, (November 29, 1966).

69. D. Babilis, P. Dais, L. H. Margaritis, C. M. Paleos*, J. Polym. Sci, Polym. Chem. Ed*, **23**, 1089(1985).

70. D. V. Valerie, E. J. Goethals, *Macromol. Rapid Commun*. **18**, 149 (1997).

71. T. Amemiya, M. Katayama and Harada, *Macromol.Chem*, **176**, 1289 (1975).

72. T. J. Suen and A. M. Schiller, *U.S.Patent3*, **171**,805 (March 2, 1965).

73. G. B. Butler and R. J. Angelo, *J.Am.Chem.Soc*, **78**, 4797 (1956).

74. G. B. Butler and R. L. Goette*, J. Am. Chem. Soc*, **76**, 2418 (1954).

75. G. B. Butler, Bunch and F. L. Ingley*, J. Am. Chem. Soc***, 74,** 2345 (1952).

76. M. F. Hooover, *J. Macromol. Sci. Chem*, **A4**, 1327, (1970).

77. H. A. J. Battaerd, *U.S.Patent3*, **619**, 394 (1971).

78. H. G. Flock, E, G Rausch, Water Soluble Polymers, N. M. Bikales, Ed Plnum Press, New York, P.42 (1973).

79. J. C. Salamone, W. Volksen, S. C. Israel, D. C. Raia*, Polym. Prepr*. **15**, 291 (1974).

80. J. C. Salamone, W. Volksen, S. C. Israel, D. C. Raia, A. Broggi, T. D. Hsu, *Polym.Prepr*, **16**, 731 (1975.)

81. R. W. Armstrong, U. P.Trauss. In Encyclopedia of Polymer Science and Technology, *Inter science, New York* **10**, 781 (1969).

82. G. W. Fischer, R. Jentzch, V. Kasanzewa and F. Riemer, *J. Prakt*. *Chem,* **317**, 943 (1975).

83. A. Laschewsky and I. Zerbe, *Polymer,* **32**, 2070 (1991)

84. M. Haln, J. Kotz, K. J. Linow and B. Philipp, *Acta Polym,* **40**, 36 (1989).

85. Y. Muroga, M. Amano, A. Katagiri, I. Noda and T. Nakaya, *Polymer J*, **27,** 65, (1995).

86. G. Ehrlich and P. Doty, *J. Am. Chem. Soc*, **76**, 3764 (1954).

87. M. Nagasawa and I. Noda, *J. Am. Chem. Soc*, **90,** 7200 (1968).

88. S. Matsumura, E. Yokochi, I. Winnnrsito, and K. Toshima, *Chem*. *Lett*, 215 (1997).

89. S. Nath, *J. Chem. Techno.and Biotechno*, **62**, 295 (1995).

90. C. Patrickios, W. Hertler, and T. A. Hatton, *Abstr.Papers of Am*. *Chem. Soc*, **207**,161 (1994).

91. E. Terlemezian, S. Veleva, and A. Arsor, *Acta.Polym*, **41**, 42 (1990).

92. Butler, G. B; Angelo, R. J; *J Am Chem. Soc*. **79**,3128(1957).

93. Barbucci, R.; Casolaro, M.; Ferruti, P.; Barone, V.; Lelji, F.; Oliva, L. *Macromolecules*, **14**, 1203 (1981).

94. Barbucci, R.; Casolaro, M.; Nocentini, M.; Correzzi, S.; Ferruti, P.; Barone, V. *Macromolecules*, **19**, 37 (1986).

95. Barbucci, R.; Casolaro, M.; Ferruti, P.; Nocentini, M. *Macromolecules*, **19**, 1856 (1986.

96. Ferruti, P.; Barbucci, R. *Adv Polym Chem.*, 58, 57 (1984).

97. Barbucci, R.; Casolaro, M.; Danzo, N.; Barone, V.; Ferruti, P.; Angeloni, A. *Macromolecules*, **16**, 456 (1983).

98. Hughes, P.; Lowe, C. R. *Enzyme Microb Technol*, **10**, 115 (1988).

99. Fetty, W.K; *J. Chem. Edu*. **55**,576 (1978)

APPENDIX [A]

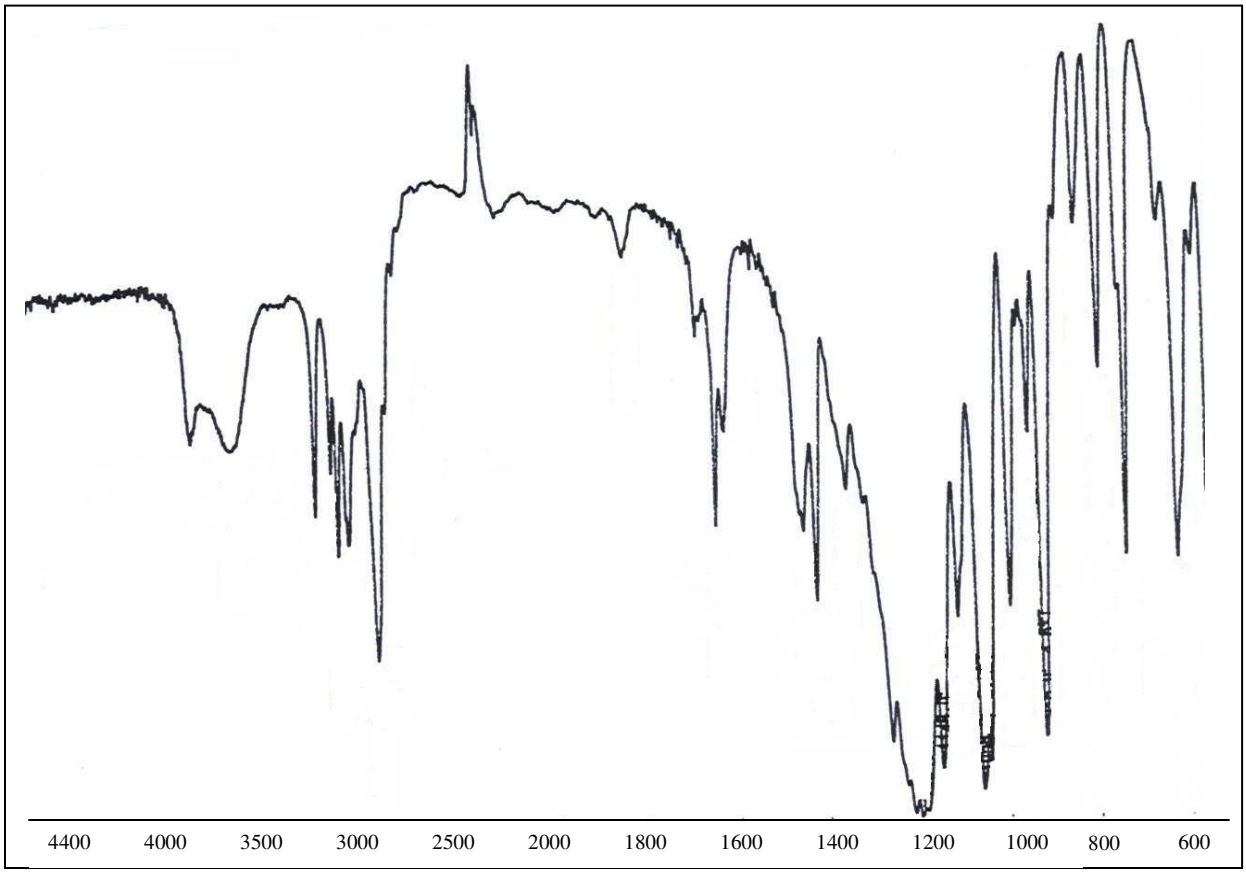


Figure A (I): FTIR Spectrum of Monomer **19** in KBr at 20 °C.

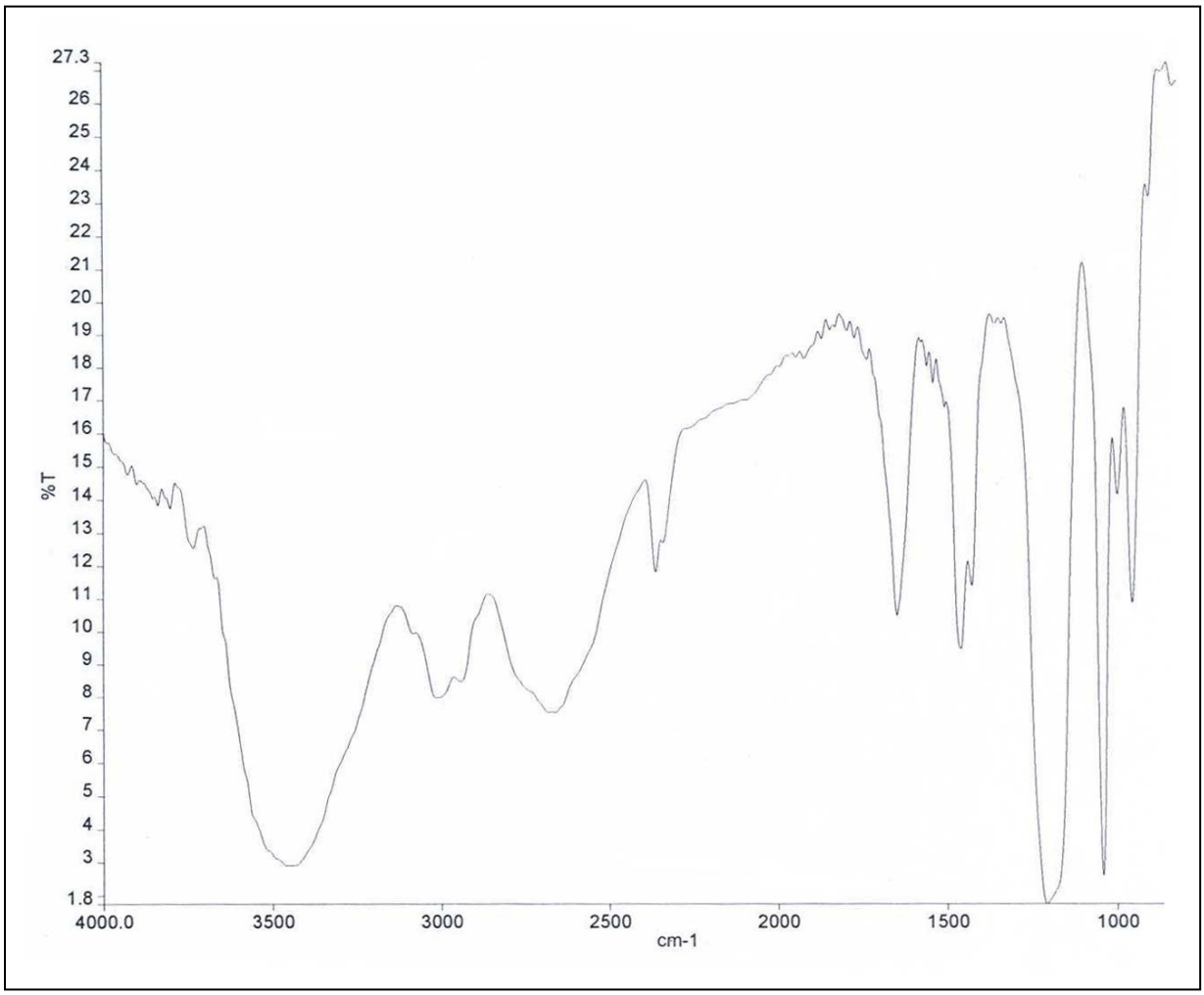


Figure A(II): FTIR Spectrum of Zwitterionic Monomer **20** in KBr at 20 °C.

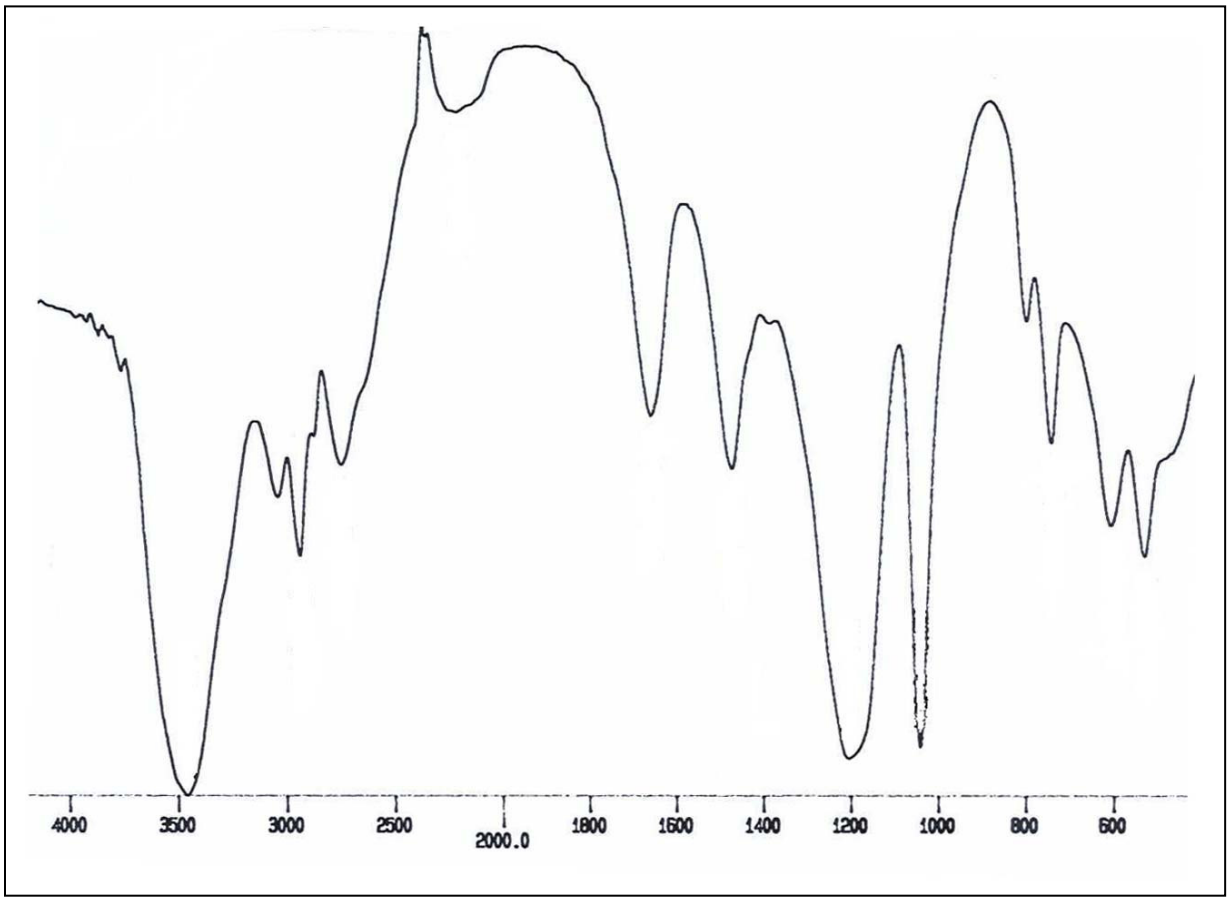


Figure A(III): FTIR Spectrum of polysulfobetaine (PSB) **21** in KBr at 20 °C.

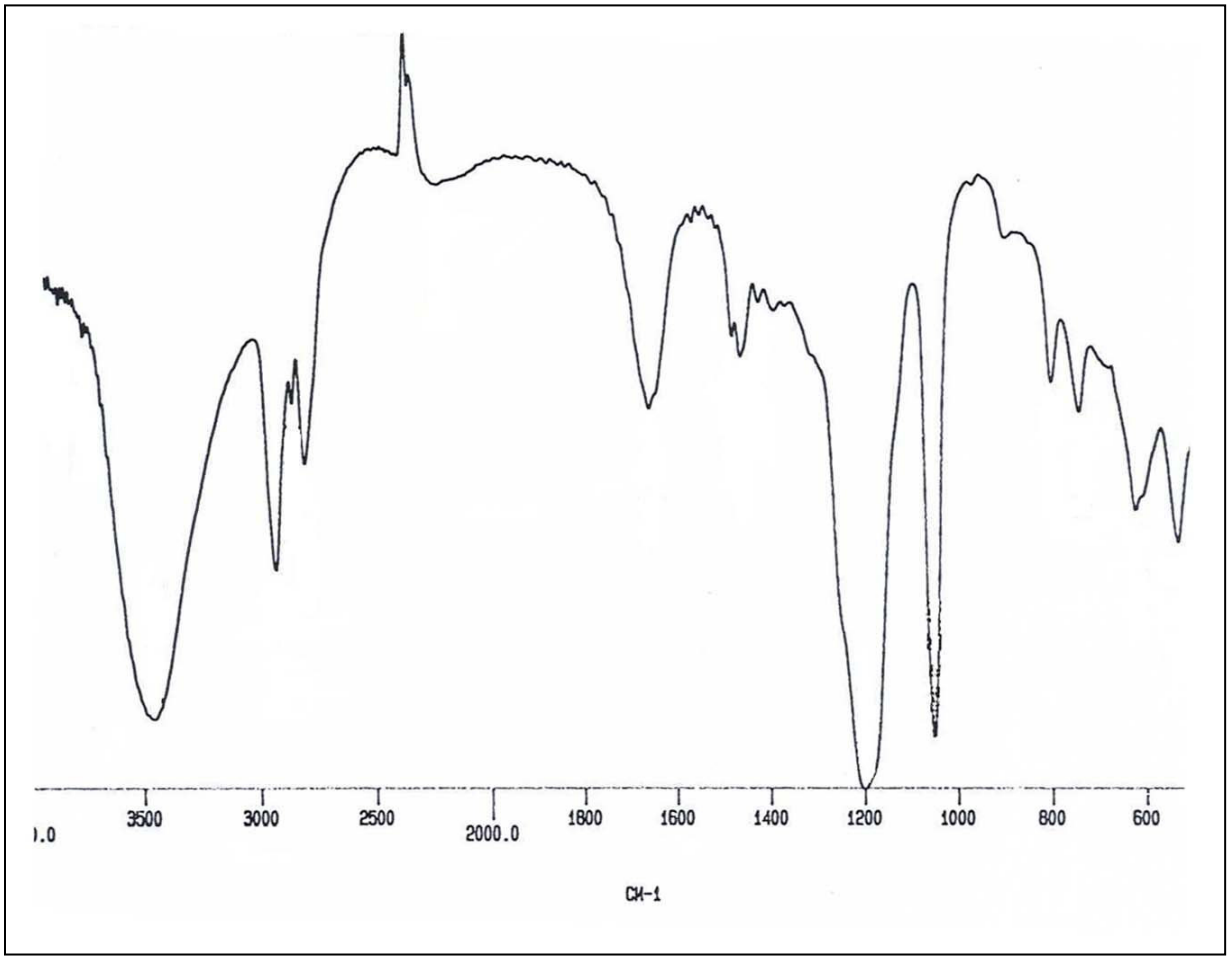


Figure A(IV): FTIR Spectrum of anionic polyelectrolyte (APE) **22** in KBr at 20 °C.

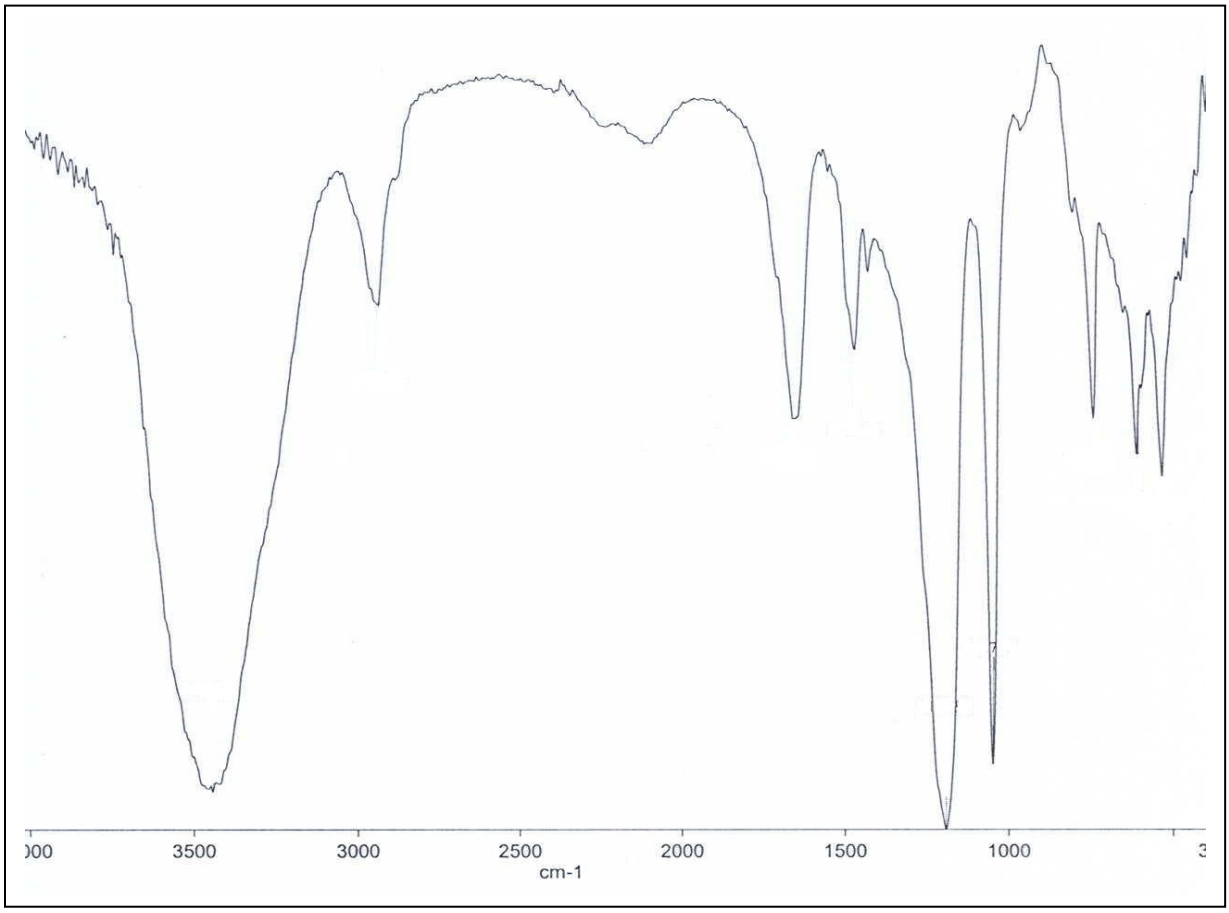


Figure A(V): FTIR Spectrum of the Zwitterionic Electrolytic Monomer **(24)** in KBr at 20 °C.

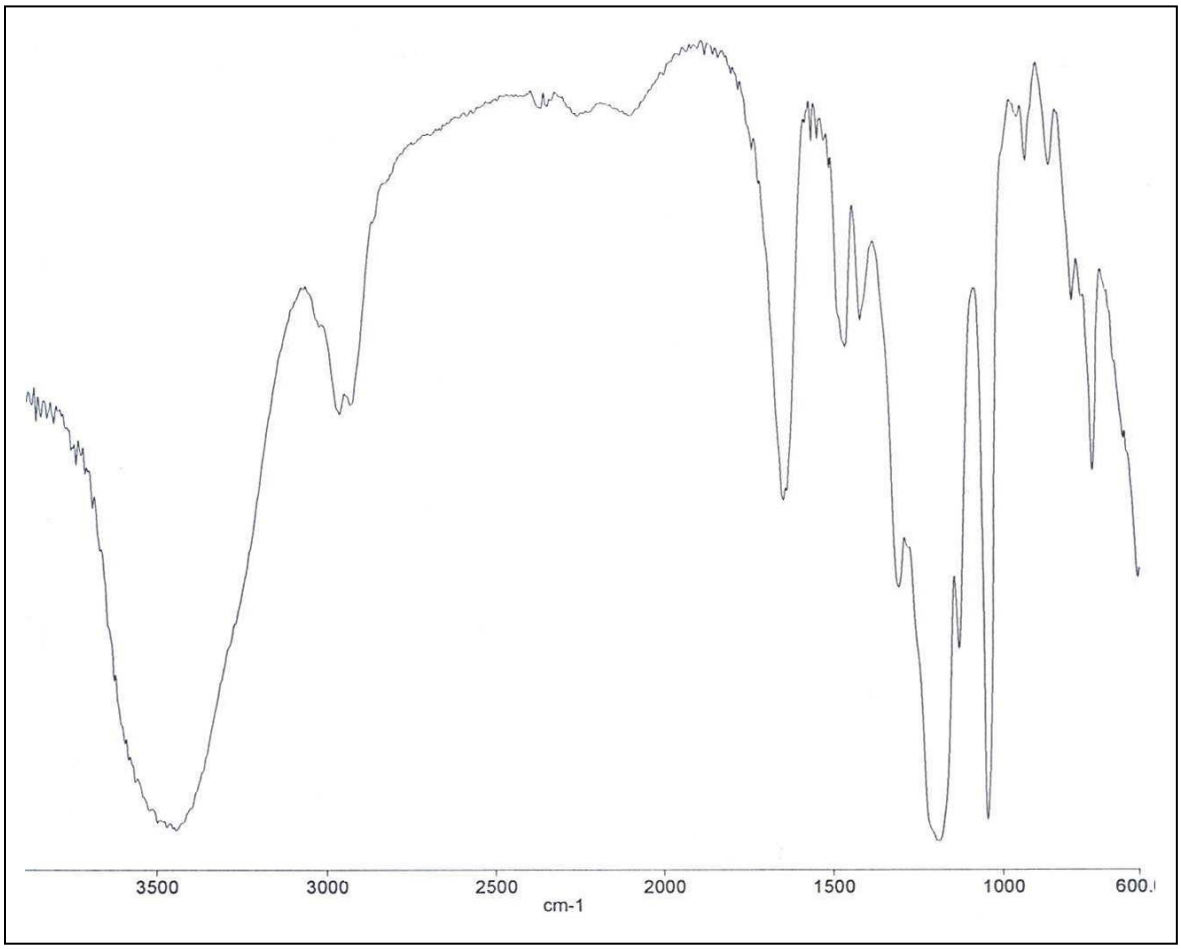


Figure A(VI): FTIR Spectrum of PEZ Homopolymer **(25)** in KBr at 20 °C.

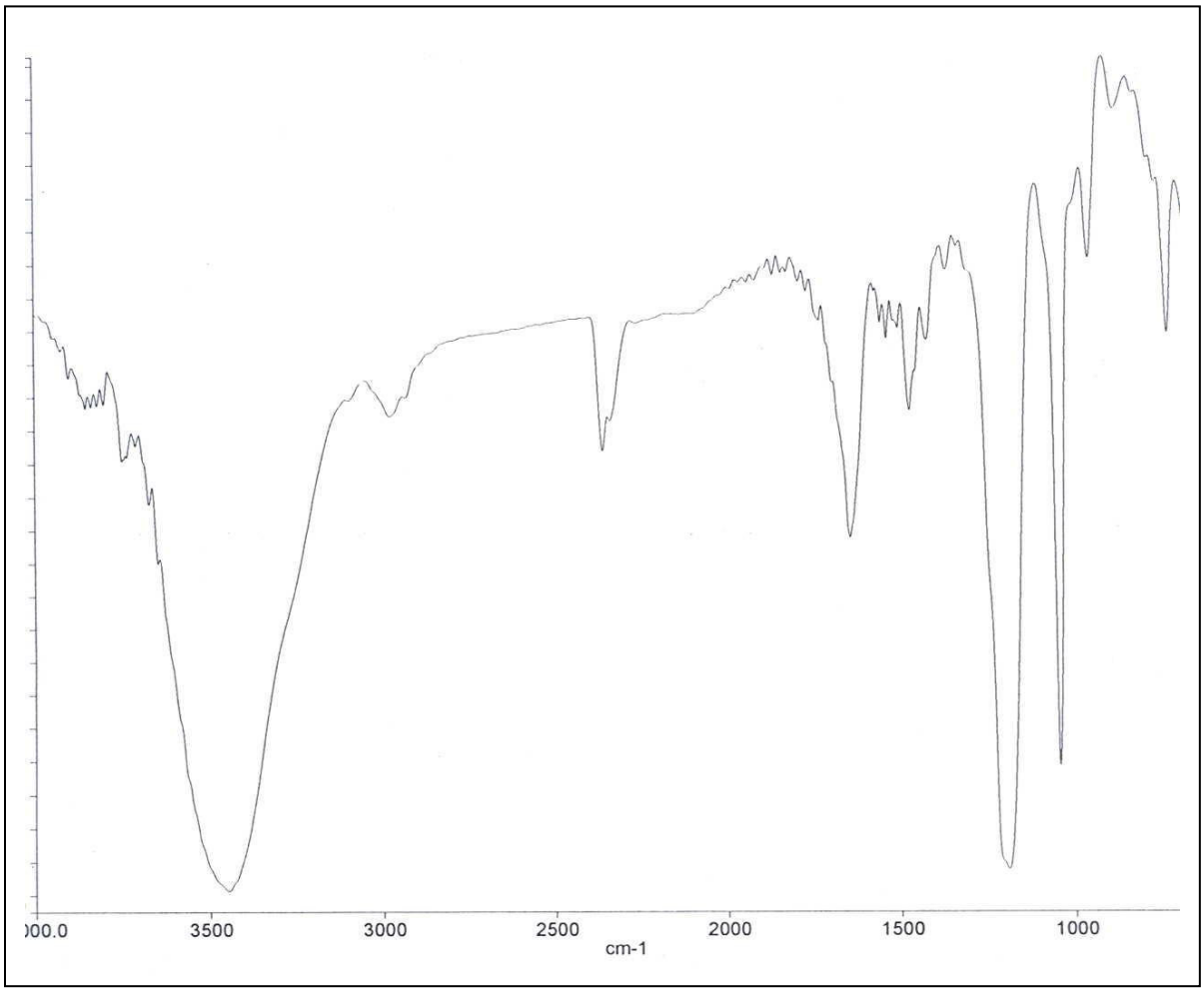


Figure A(VII): FTIR Spectrum of PEZ Copolymer **(26)** in KBr at 20 °C.

APPENDIX [B]

B(I): Protonation of the Polymer **23** ($ZH^{\pm}$) at 25 °C in salt free water and with 0.1015 HCl (Table 4,Run 2).

[a]initial vol.	Vol of HCl (0.1015 N)	Total vol.	C_H^+	H^+	OH^-	[c]$ZH^{\pm}$ = $C_H^+ - H^+ + OH^-$	[b]Z_0	[d]α = $ZH^{\pm}/Z_0$	1- α	log((1-α)/α)	pH	α	logK^e
200	0	200.00	0	0	0.001778	0.00177800	0.002485	0.715441	0.284559	-0.400402	11.25	0.715441	11.65040
200	0.25	200.25	0.000127	0	0.001585	0.001711717	0.002482	0.689631	0.310369	-0.346738	11.2	0.689631	11.54674
200	0.50	200.50	0.000253	0	0.001413	0.001666117	0.002479	0.672097	0.327903	-0.311687	11.15	0.672097	11.46169
200	0.75	200.75	0.000379	0	0.001259	0.001638203	0.002476	0.661661	0.338339	-0.291283	11.1	0.661661	11.39128
200	1.00	201.00	0.000505	0	0.001096	0.001600975	0.002473	0.647430	0.352570	-0.263947	11.04	0.647430	11.30395
200	1.25	201.25	0.000630	0	0.000933	0.001563635	0.002470	0.633116	0.366884	-0.236955	10.97	0.633116	11.20695
200	1.50	201.50	0.000756	0	0.000776	0.001531583	0.002467	0.620909	0.379091	-0.214284	10.89	0.620909	11.10428
200	1.75	201.75	0.000880	0	0.000646	0.001526121	0.002464	0.619462	0.380538	-0.211617	10.81	0.619462	11.02162
200	2.00	202.00	0.001005	0	0.000447	0.001451650	0.002461	0.589964	0.410036	-0.158004	10.65	0.589964	10.80800
200	2.25	202.25	0.001129	0	0.000347	0.001475872	0.002458	0.600550	0.399450	-0.177087	10.54	0.600550	10.71709
200	2.50	202.50	0.001253	0	0.000275	0.001528486	0.002454	0.622729	0.377271	-0.217645	10.44	0.622729	10.65764
200	2.75	202.75	0.001377	0	0.000214	0.001590495	0.002451	0.648792	0.351208	-0.266541	10.33	0.648792	10.59654
200	3.00	203.00	0.001500	0	0.000162	0.001662200	0.002448	0.678878	0.321122	-0.325121	10.21	0.678878	10.53512
200	3.25	203.25	0.001623	0	0.000110	0.001732601	0.002445	0.708502	0.291498	-0.385706	10.04	0.708502	10.42571
200	3.50	203.50	0.001746	0	7.76E-05	0.001823320	0.002442	0.746517	0.253483	-0.469090	9.89	0.746517	10.35909
200	3.75	203.75	0.001868	0	4.9E-05	0.001917078	0.002439	0.785868	0.214132	-0.564668	9.69	0.785868	10.25467
200	4.00	204.00	0.001990	0	3.31E-05	0.002023306	0.002436	0.830432	0.169568	-0.689959	9.52	0.830432	10.20996
200	4.25	204.25	0.002112	0	1.95E-05	0.002131495	0.002433	0.875908	0.124092	-0.848715	9.29	0.875908	10.13872
200	4.50	204.50	0.002233	0	7.94E-06	0.002241439	0.002430	0.922216	0.077784	-1.073940	8.9	0.922216	9.973940
200	4.75	204.75	0.002355	0	1.59E-06	0.002356286	0.002428	0.970653	0.029347	-1.519502	8.2	0.970653	9.719502
200	5.00	205.00	0.002476	1.23E-06	0	0.002474380	0.002425	1.020545	-0.020550		5.91	1.020545	

[a]0.4970 mmol of polysulfobetaine **23** is treated with 1 equivalent (4.75 cm^3) of 0.1046 N NaOH, and volume is made to 200 cm^3 by adding the deionized water (192.2 cm^3) and the resultant APE **24** is then titrated with 0.1015 N HCl by continuous stirring at 25 °C .

[b]Z_0 is the initial analytical concentration of the monomeric units.

[c]$ZH^{\pm}$ is the concentration of the protonated species at the equilibrium.

[d]α is the degree of protonation.

[e]logK is the basicity constant.

B(II): Protonation of the Anionic Polymer (APE) **24** (Z^-) at 25 °C in salt free water and with 0.1015 HCl (Table 4,Run 4).

[a]initial vol	Vol of HCl (0.1015 N)	Total vol.	C_H^+	H^+	OH^-	[c]$ZH^{\pm}$ = $C_H^+ - H^+ + OH^-$	[b]Z_0	[d]α = $ZH^{\pm}/Z_0$	1- α	log((1-α)/α)	pH
200	0	200.00	0	0	0.001380	0.00138	0.002318	0.595397	0.404603	-0.167778	11.14
200	0.25	200.25	0.000127	0	0.001230	0.0013567	0.002315	0.586083	0.413917	-0.151047	11.09
200	0.50	200.50	0.000253	0	0.001096	0.0013491	0.002312	0.583528	0.416472	-0.146476	11.04
200	0.75	200.75	0.000379	0	0.000933	0.0013122	0.002309	0.568270	0.431730	-0.119342	10.97
200	1.00	201.00	0.000505	0	0.000813	0.0013178	0.002306	0.571393	0.428607	-0.124876	10.91
200	1.25	201.25	0.000630	0	0.000676	0.0013064	0.002303	0.567181	0.432819	-0.117415	10.83
200	1.50	201.50	0.000756	0	0.000550	0.0013051	0.002301	0.567298	0.432702	-0.117622	10.74
200	1.75	201.75	0.000880	0	0.000447	0.0013271	0.002298	0.577593	0.422407	-0.135891	10.65
200	2.00	202.00	0.001005	0	0.000347	0.0013517	0.002295	0.588998	0.411002	-0.156269	10.54
200	2.25	202.25	0.001129	0	0.000269	0.0013982	0.002292	0.610024	0.389976	-0.194309	10.43
200	2.50	202.50	0.001253	0	0.000200	0.0014526	0.002289	0.634548	0.365452	-0.239635	10.30
200	2.75	202.75	0.001377	0	0.000132	0.0015085	0.002286	0.659785	0.340215	-0.287650	10.12
200	3.00	203.00	0.001500	0	9.55E-05	0.0015955	0.002284	0.698700	0.301300	-0.365291	9.98
200	3.25	203.25	0.001623	0	6.46E-05	0.0016876	0.002281	0.739925	0.260075	-0.454090	9.81
200	3.50	203.50	0.001746	0	4.27E-05	0.0017884	0.002278	0.785086	0.214914	-0.562652	9.63
200	3.75	203.75	0.001868	0	3.02E-05	0.0018983	0.002275	0.834372	0.165628	-0.702227	9.48
200	4.00	204.00	0.001990	0	1.51E-05	0.0020053	0.002272	0.882483	0.117517	-0.875607	9.18
200	4.25	204.25	0.002112	0	7.08E-06	0.0021191	0.002270	0.933698	0.066302	-1.148676	8.85
200	4.50	204.50	0.002233	0	0	0.0022335	0.002267	0.985318	0.014682	-1.826787	7.35
200	4.75	204.75	0.002355	3.09E-06	0	0.0023516	0.002264	1.038693	-0.038690		5.51
200	5.00	205.00	0.002476	6.76E-05	0	0.002408	0.002261	1.064903	-0.064900		4.17
200	5.25	205.25	0.002596	0.000178	0	0.0024184	0.002258	1.070812	-0.070810		3.75

[a]0.463557 mmol of anionic polyelectrolyte (APE) **24** is dissolved in deionized water to make the volume 200 cm^3 and then titrated with 0.1015 N HCl by continuous stirring at 25 °C.

[b]Z_0 is the initial analytical concentration of the monomeric units.

[c]$ZH^{\pm}$ is the concentration of the protonated species at the equilibrium.

[d]α is the degree of protonation.

B (III): Protonation of the Monomer **19** (Z_0) at 25 °C in salt free water and with 0.1015 HCl (Table 4, Run 1).

[a]initial vol.	Vol of HCl (0.1015 N)	Total vol	C_H^+	H^+	OH^-	[c]$ZH^{\pm}$ = $C_H^+ - H^+ + OH^-$	[b]Z_0	[d]α = $ZH^{\pm}/Z_0$	1- α	log((1-α)/α)	pH
207.22	0	207.22	0	0	4.47E-05	0.00004467	0.001514	0.029504	0.97050	1.517120	9.65
207.22	0.25	207.47	0.000122	0	2.69E-05	0.00014923	0.001512	0.098680	0.90132	0.960651	9.43
207.22	0.50	207.72	0.000244	0	1.45E-05	0.00025877	0.001510	0.171324	0.82868	0.684568	9.16
207.22	0.75	207.97	0.000366	0	0.00001	0.00037604	0.001509	0.249264	0.75074	0.478829	9.00
207.22	1.00	208.22	0.000487	0	6.92E-06	0.00049438	0.001507	0.328104	0.67190	0.311289	8.84
207.22	1.25	208.47	0.000609	0	4.79E-06	0.00061339	0.001505	0.407572	0.59243	0.162432	8.68
207.22	1.50	208.72	0.000729	0	3.24E-06	0.00073268	0.001503	0.487423	0.51258	0.021854	8.51
207.22	1.75	208.97	0.000850	0	2.29E-06	0.00085229	0.001501	0.567673	0.43233	-0.118287	8.36
207.22	2.00	209.22	0.000970	0	1.66E-06	0.00097193	0.001500	0.648133	0.35187	-0.265285	8.22
207.22	2.25	209.47	0.001090	0	1.12E-06	0.00109137	0.001498	0.728654	0.27135	-0.428997	8.05
207.22	2.50	209.72	0.001210	0	7.08E-07	0.00121065	0.001496	0.809256	0.19074	-0.627636	7.85
207.22	2.75	209.97	0.001329	0	3.09E-07	0.00132967	0.001494	0.889868	0.11013	-0.907412	7.49
207.22	3.00	210.22	0.001448	1.74E-07	0	0.00144831	0.001492	0.970423	0.02958	-1.516009	6.76
207.22	3.25	210.47	0.001567	3.31E-05	0	0.00153422	0.001491	0.029207	0.97079	1.521647	4.48
207.22	3.50	210.72	0.001686	0.000162	0	0.00152369	0.001489	0.023357	0.97664	1.621312	3.79
207.22	3.75	210.97	0.001804	0.000251	0	0.00155297	0.001487	0.044260	0.95574	1.334326	3.60

[a]0.31374 mmol of monomer **19** (Z_0) is dissolved in 207.22 cm^3 of deionized water and then titrated with 0.1015 N HCl by continuous stirring at 25 °C . Final calculation is done with respect to the initial volume as 200 cm^3 (0.3028 mmol of monomer).

[b]Z_0 is the initial analytical concentration of the monomeric units.

[c]$ZH^{\pm}$ is the concentration of the protonated species at the equilibrium.

[d]α is the degree of protonation.

B (IV): Protonation of the Polymer **23** ($ZH^{\pm}$) at 25 °C in 0.1N NaCl and with 0.1015 HCl (Table 4,Run 1).

[a]initial vol	Vol of HCl	Total vol.	C_H^+	H^+	OH^-	[c]$ZH^{\pm}$ = $C_H^+ - H^+ + OH^-$	[b]Z_0 A-	[d]α = $ZH^{\pm}/Z_0$	1- α	log((1-α)/α)	pH
200	0	200.00	0	0	0.0004898	0.0004898	0.001995	0.245516	0.754484	0.4875708	10.69
200	0.25	200.25	0.000127	0	0.0003981	0.0005248	0.001992	0.263397	0.736603	0.4466229	10.60
200	0.50	200.50	0.000253	0	0.0003236	0.0005767	0.001990	0.289806	0.710194	0.3892689	10.51
200	0.75	200.75	0.000379	0	0.0002512	0.0006304	0.001988	0.317179	0.682821	0.3330025	10.40
200	1.00	201.00	0.000505	0	0.0001995	0.0007045	0.001985	0.354889	0.645111	0.2595423	10.30
200	1.25	201.25	0.000630	0	0.0001514	0.0007818	0.001983	0.394350	0.605650	0.1863405	10.18
200	1.50	201.50	0.000756	0	0.0001122	0.0008678	0.001980	0.438245	0.561755	0.1078302	10.05
200	1.75	201.75	0.000880	0	0.0000813	0.0009617	0.001978	0.486278	0.513722	0.0238441	9.91
200	2.00	202.00	0.001005	0	0.0000575	0.0010625	0.001975	0.537907	0.462093	-0.0659770	9.76
200	2.25	202.25	0.001129	0	0.0000398	0.0011690	0.001973	0.592553	0.407447	-0.1626550	9.60
200	2.50	202.50	0.001253	0	0.0000275	0.0012806	0.001970	0.649947	0.350053	-0.2687450	9.44
200	2.75	202.75	0.001377	0	0.0000186	0.0013953	0.001968	0.709029	0.290971	-0.3868140	9.27
200	3.00	203.00	0.001500	0	0.0000126	0.0015126	0.001966	0.769570	0.230430	-0.5237080	9.10
200	3.25	203.25	0.001623	0	0.0000087	0.0016317	0.001963	0.831198	0.168802	-0.6923270	8.94

[a]0.3990 mmol of polysulfobetaine **23** is treated with 1 equivalent (3.85 cm^3) of 0.1046 N NaOH, and added 21.4 mg NaCl and then volume is made to 200 cm^3 by adding the 0.1N NaCl (196.2 cm^3) and the resultant APE **24** is then titrated with 0.1015 N HCl by continuous stirring at 25 °C .

[b]Z_0 is the initial analytical concentration of the monomeric units.

[c]$ZH^{\pm}$ is the concentration of the protonated species at the equilibrium.

[d]α is the degree of protonation.

B (V): Protonation of the Anionic Polymer (APE) **24** (Z^-) at 25 °C in 0.1N NaCl and with 0.1015 HCl (Table 4, Run 4).

[a]initial vol	Vol of HCl	Total vol.	C_H^+	pH	H^+	OH^-	[c]$ZH^{\pm}$ = $C_H^+ - H^+ + OH^-$	[b]Z_0	[d]α = $ZH^{\pm}/Z_0$	1- α	log ((1-α)/α)	pH
200	0	200.00	0	10.77	1.6982E-11	5.88844E-04	0.0005888	0.002584	0.227891	0.772109	0.529951	10.77
200	0.25	200.25	0.000127	10.71	1.9498E-11	5.12861E-04	0.0006396	0.002581	0.247836	0.752164	0.482149	10.71
200	0.50	200.50	0.000253	10.64	2.2908E-11	4.36516E-04	0.0006896	0.002577	0.267566	0.732434	0.437339	10.64
200	0.75	200.75	0.000379	10.56	2.7542E-11	3.63078E-04	0.0007423	0.002574	0.288351	0.711649	0.392344	10.56
200	1.00	201.00	0.000505	10.48	3.3113E-11	3.01995E-04	0.0008070	0.002571	0.313871	0.686129	0.339654	10.48
200	1.25	201.25	0.000630	10.39	4.0738E-11	2.45471E-04	0.0008759	0.002568	0.341107	0.658893	0.285924	10.39
200	1.50	201.50	0.000756	10.30	5.0119E-11	1.99526E-04	0.0009551	0.002565	0.372414	0.627586	0.226647	10.30
200	1.75	201.75	0.000880	10.20	6.3095E-11	1.58489E-04	0.0010389	0.002561	0.405592	0.594408	0.165995	10.20
200	2.00	202.00	0.001005	10.10	7.9433E-11	1.25893E-04	0.0011308	0.002558	0.442030	0.557970	0.101159	10.10
200	2.25	202.25	0.001129	9.99	1.0233E-10	9.77237E-05	0.0012269	0.002555	0.480169	0.519831	0.034468	9.99
200	2.50	202.50	0.001253	9.88	1.3182E-10	7.58578E-05	0.0013289	0.002552	0.520750	0.479250	-0.036068	9.88
200	2.75	202.75	0.001377	9.76	1.7378E-10	5.75440E-05	0.0014342	0.002549	0.562704	0.437296	-0.109505	9.76
200	3.00	203.00	0.001500	9.65	2.2387E-10	4.46684E-05	0.0015447	0.002546	0.606777	0.393223	-0.188390	9.65
200	3.25	203.25	0.001623	9.52	3.0199E-10	3.31131E-05	0.0016561	0.002543	0.651356	0.348644	-0.271437	9.52
200	3.50	203.50	0.001746	9.40	3.9811E-10	2.51189E-05	0.0017708	0.002539	0.697327	0.302673	-0.362462	9.40
200	3.75	203.75	0.001868	9.27	5.3703E-10	1.86209E-05	0.0018867	0.002536	0.743880	0.256120	-0.463058	9.27
200	4.00	204.00	0.001990	9.15	7.0794E-10	1.41254E-05	0.0020043	0.002533	0.791216	0.208784	-0.578599	9.15
200	4.25	204.25	0.002112	9.00	1.0000E-09	1.00000E-05	0.0021220	0.002530	0.838695	0.161305	-0.715957	9.00
200	4.50	204.50	0.002233	8.89	1.2882E-09	7.76247E-06	0.0022413	0.002527	0.886917	0.113083	-0.894486	8.89

[a]0.516776 mmol of anionic polyelectrolyte (APE) **24** is dissolved in 0.1N NaCl to make the volume 200 cm^3 and then titrated with 0.1015 N HCl by continuous stirring at 25 °C .

[b]Z_0 is the initial analytical concentration of the monomeric units.

[c]$ZH^{\pm}$ is the concentration of the protonated species at the equilibrium.

[d]α is the degree of protonation

B (VI): Protonation of the Monomer **19** (Z_0) at 25 °C in 0.1N NaCl and with 0.1015 HCl (Table 4, Run 3).

[a]initial vol.	Vol of HCl	Total vol	C_H^+	pH	H^+	OH^-	[c]$ZH^{\pm}$ = $C_H^+ - H^+ + OH^-$	[b]Z_0	[d]α = $ZH^{\pm}/Z_0$	1- α	log((1-α)/α)	pH
200.83	0	200.83	0	9.67	0	4.68E-05	4.67735E-05	0.002570	0.018197	0.981803	1.732018	9.67
200.83	0.25	201.08	0.000126	9.42	0	2.63E-05	0.000152496	0.002567	0.059403	0.940597	1.199600	9.42
200.83	0.50	201.33	0.000252	9.25	0	1.78E-05	0.000269857	0.002564	0.105249	0.894751	0.929483	9.25
200.83	0.75	201.58	0.000378	9.09	0	1.23E-05	0.000389944	0.002561	0.152275	0.847725	0.745627	9.09
200.83	1.00	201.83	0.000503	8.97	0	9.33E-06	0.000512231	0.002558	0.200276	0.799724	0.601311	8.97
200.83	1.25	202.08	0.000628	8.86	0	7.24E-06	0.00063509	0.002554	0.248620	0.751380	0.480323	8.86
200.83	1.50	202.33	0.000752	8.76	0	5.75E-06	0.000758238	0.002551	0.297196	0.702804	0.373790	8.76
200.83	1.75	202.58	0.000877	8.66	0	4.57E-06	0.000881385	0.002548	0.345892	0.654108	0.276710	8.66
200.83	2.00	202.83	0.001001	8.56	0	3.63E-06	0.001004469	0.002545	0.394681	0.605319	0.185738	8.56
200.83	2.25	203.08	0.001125	8.45	0	2.82E-06	0.001127375	0.002542	0.443520	0.556480	0.098536	8.45
200.83	2.50	203.33	0.001248	8.37	0	2.34E-06	0.001250316	0.002539	0.492492	0.507508	0.013044	8.37
200.83	2.75	203.58	0.001371	8.28	0	1.91E-06	0.001372988	0.002536	0.541477	0.458523	-0.072218	8.28
200.83	3.00	203.83	0.001494	8.19	0	1.55E-06	0.001495441	0.002533	0.590493	0.409507	-0.158954	8.19
200.83	3.25	204.08	0.001616	8.08	0	1.20E-06	0.001617603	0.002529	0.639514	0.360486	-0.248962	8.08
200.83	3.50	204.33	0.001739	7.98	0	9.55E-07	0.001739564	0.002526	0.688574	0.311426	-0.344595	7.98
200.83	3.75	204.58	0.001861	7.85	0	7.08E-07	0.001861227	0.002523	0.737633	0.262367	-0.448931	7.85
200.83	4.00	204.83	0.001982	7.69	0	4.90E-07	0.001982621	0.002520	0.786704	0.213296	-0.566828	7.69
200.83	4.25	205.08	0.002103	7.52	0	3.31E-07	0.002103779	0.002517	0.835798	0.164202	-0.706722	7.52
200.83	4.50	205.33	0.002224	7.24	0	1.74E-07	0.002224642	0.002514	0.884892	0.115108	-0.885785	7.24
200.83	4.75	205.58	0.002345	6.74	2E-07	0	0.002345012	0.002511	0.933907	0.066093	-1.150150	6.74
200.83	5.00	205.83	0.002466	5.49	3E-06	0	0.002462391	0.002508	0.981846	0.018154	-1.733077	5.49

[a]0.51621 mmol of monomer **19** (Z_0) is dissolved in 200.83 cm^3 of 0.1N NaCl and then titrated with 0.1015 N HCl by continuous stirring at 25 °C .

Final calculation is done with respect to the initial volume as 200 cm^3 (0.5141 mmol of monomer).

[b]Z_0 is the initial analytical concentration of the monomeric units.

[c]$ZH^{\pm}$ is the concentration of the protonated species at the equilibrium.

[d]α is the degree of protonation.

Resume

of

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Publications:

- Sk. Ashrof Ali, Mohammad A.J.Mazumder, Hasan A.Al-Muallem, "Synthesis and Solution Properties of a New pH- Responsive Polymer Containing Amino Propanesulfonic acid Residues" **Journal of Polymer Science: Part A Vol. 41, 172-184 (2003)**
- Sk. Ashrof Ali, Hasan A.Al-Muallem, Mohammad A.J.Mazumder, " Synthesis and Solution Properties of a New Sulfobetaine/Sulfur dioxide Copolymer and its use in aqueous two- phase polymer systems" **Polymer, Vol. 44, 1671-1679 (2003)**
- Mohammad A.J.Mazumder, Sk. Ashrof Ali, "Synthesis and Solution Properties of a new Poly(Electrolyte- Zwitterions)" **Manuscript under preparation**.